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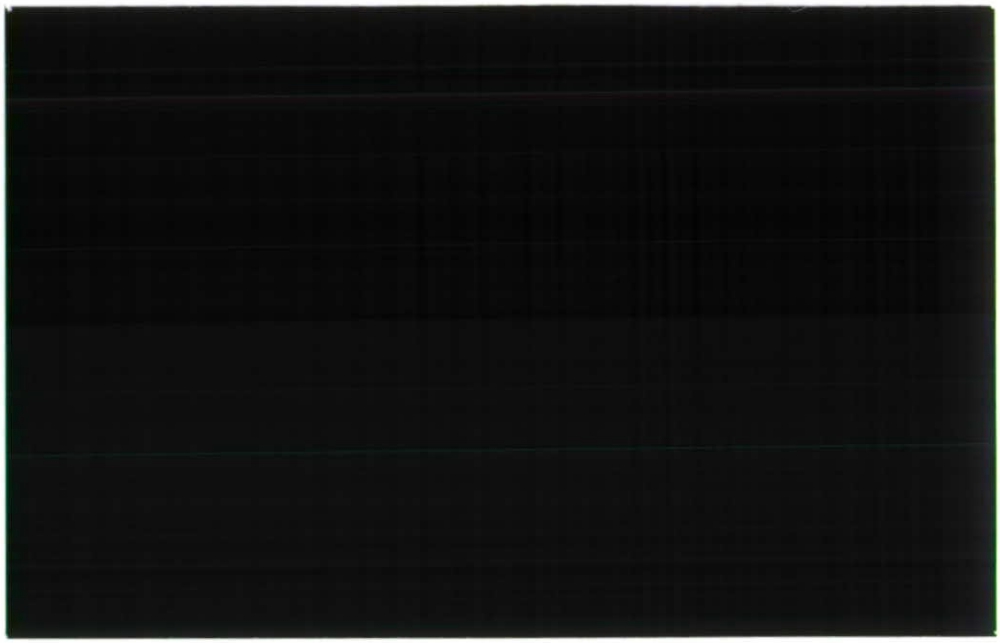

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Pesticide Briefing Note

prepared by

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Contents

1 Environmental fate of pesticides

The main pathways which pesticides can follow through the environment are shown in figure 1. An brief description of the pathways between the environmental compartments and the reactions that occur within them, are given below.

Pesticide Application
Pesticides sprayed on fields are intercepted by the crop, lost as spray drift and deposited on the soil surface. The amount of spray drift is dependent on the mechanical sprayer being used and the wind conditions. Reduction of spray drift is important since it represents both a financial waste to the farmer and a potential threat to non target organisms.

Soil and Soil Water
Pesticide which is deposited on the soil may be lost to the atmosphere through volatilization. The amount volatilized varies between different pesticides and is controlled by the vapour pressure of the pesticide. Pesticide remaining in the soil will partition between the soil and the soil water; the ratio of the concentration in the soil to the concentration in the water is called the partition coefficient.

$$Kp = Cs / Cw$$

where Cs is the mass of pesticide adsorbed to a unit mass of soil (M/M) and Cw is the mass of pesticide per unit volume of soil water (M/L^3), and Kp is the partition coefficient $(M/M)/(M/L^3)$. A linear relationship has been shown to exist between the organic carbon content of a natural soil and Kp. This has led to the definition of the partition coefficient normalized on organic carbon fraction, Koc, which is independent of soil type for a given pesticide.

$$Kp = Koc * OC$$

where OC is the organic carbon content of the soil (M/M). A useful property of the Koc, is that it is linearly correlated to the octanol-water partition coefficient Kow. The Kow for a pesticide can be measured easily in the laboratory by shaking a pesticide in a known mixture of equal volumes of octanol and water and measuring the amounts of the compound in each solvent. The Kow is the ratio of the concentration in octanol to the concentration in water.

Pesticide is lost from the soil environment through transport of water; uptake by plants, runoff to rivers and leaching to groundwater, and by microbial degradation.

Degradation
This is the primary route for removal of pesticide from the environment. The majority of a pesticide applied to the soil will remain there, either attached to the soil or dissolved in the soil water. Naturally occurring microbes in the soil are able to produce enzymes that can breakdown pesticides into smaller molecules. The degradation process is usually characterized as a first order decay reaction in which the rate of loss of pesticide is proportional to the pesticide concentration. The different decay rates for individual pesticides are described by quoting a half-life. This is the amount of time it takes for the concentration of a pesticide to decrease by 50%. The half life of a pesticide has been shown to change with temperature, soil water content and soil organic carbon content.

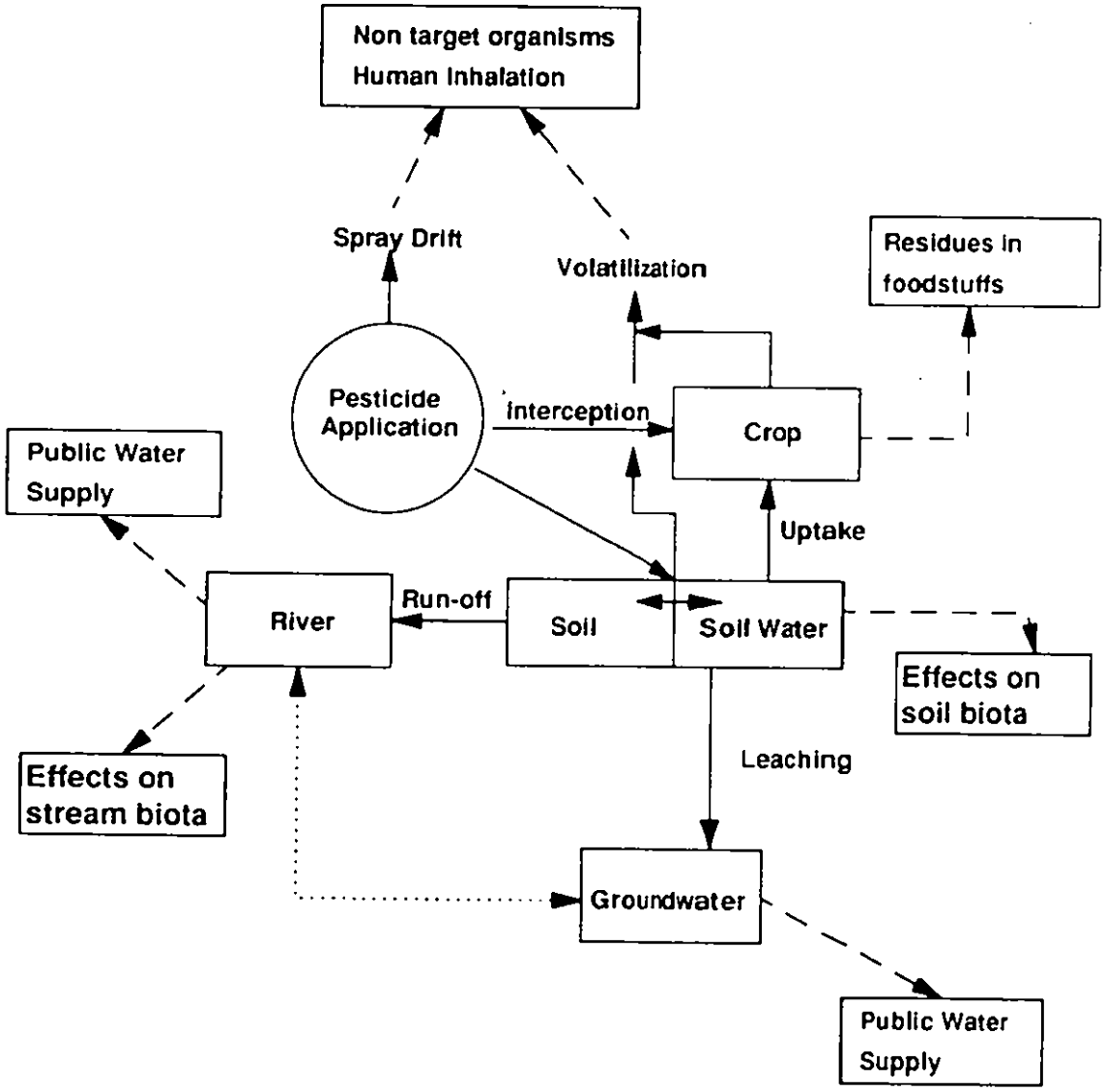

Figure 1 *Pesticide transport pathways in the environment*

The metabolytes created by the degradation of the parent pesticides are sometimes persistent (e.g. DDE, DDD from DDT) or at least more persistent than their parent (e.g. Aldicarb sulphoxide from aldicarb). The degradation products of more modern compounds are more likely to be less toxic than their parents given that manufactures are more aware nowadays of potential problems and screen for them during development.

Run-off

This term describe the lateral movement of water either over the surface or through the top layers of the soil to a water course. Run-off occurs on sloping fields when either rainfall intensity exceeds the acceptance capacity of the soil or rain falls on an already saturated soil. In poorly draining soils, artificial drainage systems maybe installed to reduce water logging by moving water more rapidly away from the soil surface. Water entering streams from such systems may also be considered to be run-off. The amount of pesticide leaving the soil by this route is greatest during rainfall events and has been shown to be generally less that 1% of that applied in individual rainfall events (Wauchope, 1978; Williams and Volkner, 1994, (enclosed)). However, these small amounts can lead to concentrations well in excess of the 0.1 µg/l laid down as the maximum acceptable concentration (MAC) by the European Union (EU). Recently the influence of macro-pores on pesticide concentrations has received increased attention. A macro-pore is a planar or tubular pore which traverses the soil and is created by a secondary influence (eg earth worms, old root channels). Being of large diameter they have the capacity to move water rapidly through the soil profile allowing pesticides to by-passing the soil matrix, where they might have been expected to be adsorbed or degraded, and thus reach drainage systems in higher concentrations. This subject has been discussed by Johnson et al (1993, (enclosed)).

Leaching

This is the vertical movement of dissolved pesticides down a soil profile as a result of a downward potential gradient caused by the infiltration of rain at the surface. The rate of movement of water through the profile is controlled by the hydraulic conductivity of the soil and the potential gradient, known as Darcy's Law. The hydraulic conductivity will be different for different soils and will also vary for individual soils depending on their water content. Pesticides dissolved in the water tend to move more slowly than the water as they are subject to sorption on to the soil and degradation. In principle, the vertical movement of a pesticide should be so slow, as compared to its half life, that little pesticide should penetrate to groundwater (unless the groundwater is very shallow). However, the presence of macro-pores (as described above) may allow a more rapid vertical movement than would be expected from classical darcian flow. Indeed small pesticides in low concentrations have been found in the groundwater in East Anglia, UK which are presumed to have moved via fissures in the chalk rocks that make up an important part of the aquifer in this area.

Uptake

Plants take up water through their roots from the soil as they grow. In doing so they take up the pesticide that is dissolved in the water. However, since the pesticide molecules are larger than water some fail to penetrate the cell walls of the roots and the effective concentration seen by the plant is reduced. Once in the plant many pesticides are metabolised by the plant and breakdown. Thus the concentration of pesticide in a plant may vary enormously through the year. After rainfall it is easy for plants to extract water from the soil and so the pesticide concentration increases. As the soil dries out the rate of pesticide uptake is reduced until it is less than the rate at which it is metabolized in the plant and the concentration falls.

Rivers

There is little information on the fate of pesticides once they enter watercourses. It is likely that there will be an interaction with the suspended load within the water column which may result in a reduction of the dissolved pesticide load and eventual settlement of pesticide on the river bed. This settled particulate pesticide has the potential to be reintroduced into the water column at high flows. The residence times in rivers is generally short compared to the microbial degradation rate of pesticides and therefore this is unlikely to affect the concentrations significantly. Other degradation route are available, including photolysis, hydrolysis and oxidation, which may act at a shorter time scale.

Groundwater

If pesticides get into groundwater it is unlikely that they will undergo any further attenuation. Populations of microbes at this depth are very small, if not non-existent, and so little degradation will occur. There is little or no organic matter in the rock that comprise most aquifers and therefore there will be negligible sorption of the chemical. Once groundwater supplies become contaminated it will take many years to restore them to their pristine state. If the groundwater is used for public supply, large expense will be incurred by water companies who may be required to treat the water or develop new resources.

The processes and pathways described above has been reviewed briefly by Johnson et al (1993, Annex 1 (enclosed)). In particular, this review discusses the processes of by-pass flow.

Bioaccumulation

Bioaccumulation is the total bio-uptake of pesticides by an organism from food items as well as via mass transport of dissolved organics through the gill and epithelium. In some circumstances bioaccumulation causes an increase in total body burden as one proceeds up the food chain from primary producer to top carnivore. This most often occurs when un-metabolised hydrophobic compounds accumulate in the fatty tissues of animals. The tendency of a compound to accumulate in this way has been found to be related to the Kow of the pesticide. The higher the Kow the more likely is the pesticide to bioaccumulate.

References (not enclosed)

Wauchope, R D, 1978, The pesticide content of surface waters draining from agricultural fields - a review, J. Environ. Qual.,7, 459-472.

2 Current pesticide research

The following is an overview of the current research that is being carried out in the UK on pesticide fate and behaviour. There is a great deal of research in this area and this list should be considered indicative of the areas being covered rather than exhaustive. The section has been organized by research organization although many projects are collaborative ventures between organizations.

Natural Environment Research Council (NERC)
The vast majority of research in NERC is carried out in four laboratories; the Institute of Hydrology (IH), the Institute of Terrestrial Ecology (ITE), the Institute of Freshwater Ecology (IFE) and the Hydrogeology Research Group within the British Geological Survey.

IH has just finished a major catchment study, based at ADAS Rosemaund, Herefordshire in collaboration with the National River Authority (NRA), the Ministry of Agriculture Fisheries and Food (MAFF) and the Building Research Establishment (BRE) (Williams and Volkner, 1993 (enclosed)). Pesticide runoff from this agricultural catchment was monitored during rainfall events and the amounts transported to the drains and the stream were related back to pesticide applications. The study showed a rapid link between the commencement of rainfall and the occurrence of pesticide in receiving waters. The amount of pesticide running off in each rainfall event was usually less than 1% of that applied but produced short lived peaks far in excess of the EU MAC and in one case at a level toxic to bioassay organisms in the stream. Mathematical models of the rainfall induced pesticide runoff have been calibrated and validated on the data set produced from the study.

The work at Rosemaund highlighted the importance of understanding the pathways and processes that control pesticide runoff. As a result a detailed field/plot experiment was set up at the Oxford University Farm (Wytham) as part of a collaboration with the Soil Survey and Land Research Centre (SSLRC) and Horticultural Research International (HRI) (Johnson et al., 1993 (enclosed)).The experiment boasts a unique combination of equipment for monitoring both chemical movement and in situ soil water conditions during and between rainfall events. This study has shown the importance of by-pass flow in moving pesticides from the soil surface to sub-surface drainage systems.

IFE have a number of research projects studying pesticide behaviour. In particular, they have been studying the interaction between particulate and dissolved pesticide transport in river systems, one of the few studies looking at in-river processes (House and Rae, 1993 (enclosed)). They have shown that sediment composition exerts a powerful influence on pesticide transport and concentrations, and that geology may be a good and rapid guide in assessing this influence.

Other work at IFE includes work on permethrin for the EU through the Bureau of Reference Materials and the occurrence of specific pesticides in river fishes. The laboratory has an on-going programme for the development of analytical methods for pesticide in complex matrices (eg river sediments).

ITE pesticide research is directed towards the effect of pesticides on flora and fauna. Long term data on pesticide levels in predatory birds has shown how their decline has been brought about by bioaccumulation of organo-chlorine insecticides. One of the

causes being the reduction of shell wall thickness in eggs produced by birds with high residues.

ITE have also researched spray drift and have been able to define buffer zones between areas sprayed and certain sensitive organisms of mainly conservation interest. Preliminary work on agriculturally beneficial organisms has been undertaken with bees. Recently (in collaboration with the University of Reading) they have undertaken a study into the synergistic effects of pesticides; the increased toxicity of mixtures of pesticides above that expected by adding their individual toxicities.

Non- agricultural uses of pesticides have been studied. In particular novel and difficult work has been done on the effect of timber treatments on bats. Second generation rodenticides are causing some problems to owls despite their use being limited to indoors. It is presumed that part-poisoned rats leave buildings and are easy prey for owls.

BGS have recently completed work for the NRA on the pollution of aquifers from diffuse pollution, with particular emphasis on the development of groundwater protection zones. A follow on from this work is a new study on the mechanisms of groundwater pollution being carried out jointly with IH.

MAFF/Agricultural Development and Advisory Service (ADAS)

The majority of the pesticide research projects within MAFF are carried out through funding of ADAS managed studies. Several studies of this nature are concerned with the runoff of pesticides from agricultural fields and farms. A catchment scale approach has been adopted at Swavsey, Cambridgeshire which operates along similar line to the IH Rosemaund Study. Additionally this project looks at land taken out of production as part of the Set-a-side programme, both on its influence on pesticide runoff and diversity of fauna (with ITE). Plot experiments have been conducted at Cockle Farm with the University of Newcastle and at Brimstone Farm with Rothamstead Experimental Station (RES). At Brimstone studies include the effects on pesticide transport of agricultural management practice and pesticide sorption and degradation.

ADAS are also looking at the use of lysimeters to develop protocols for pesticide registration, along similar line to those used in Germany.

The Boxworth project looked at the philosophy behind pesticide application and compared insurance spraying with spraying only when necessary. The comparison included effects on wildlife within the farm as well as at yield and profitability.

Water Research Centre (WRc)

WRc have carried out a study for the NRA on pesticide concentrations within a large catchment used for water supply. Concentrations were measured in rivers, groundwater and rainfall. Because of the size of the catchment they could only estimate pesticide application amounts. It was clear from the study that non-agricultural use of Atrazine and Simazine (now banned in the UK) were to blame for their wide spread occurrence in the catchment.

WRc have on-going work on developing multi-residue analytical methods for pesticides. Additionally they investigate methods of pesticide removal/treatment (eg activated carbon filters, air stripping) for raw waters for public supply.

Soils Survey and Land Research Centre (SSLRC)
SSLRC have an EU contract with HRI and several European partners to compare the accuracy of a range of mathematical models of pesticide movement. They are working with WRc to produce groundwater vulnerability maps. The maps are based on a hydrological classification scheme for soils (HOST, Hydrology of Soil Types developed with IH) and include depth to aquifer and pesticide phyisico-chemical properties.

European Science Foundation (ESF)
The ESF have a programme on Environmental Damage and its Assessment which includes consideration of organic compounds. A number of working groups have been set up under this programme covering topics ranging from Exposure Prediction to Toxicology. The eventual aim of these working groups is to provide common guidelines that might be used across Europe for the assessment and prediction of environmental damage.

3 Areas requiring investigation

There are still many aspects of pesticide fate and behaviour that require further investigation. The following are some ideas that are of hydrological interest.

a) The Behaviour of Pesticide Intercepted by a Crop. How much is retained on the crop surface? Is this pesticide degraded or is it available to be washed off on to the soil during the next rainfall event.

b) Agricultural Practice and Pesticide Transport. How do different aspects of agricultural practice (eg different methods of seed bed preparation) effect pesticide transport by, for example, altering water pathways through the soil? How does incorporation of crop residues in to the soil or additions of manure influence pesticide retention in the soil? How do different formulations of pesticide (eg adjuvants), or different delivery methods (eg pellets, wettable powders) influence pesticide transport? Addressing these questions may assist in suggesting methods, other than reducing pesticide usage, to be investigated as tools for reducing pesticide contamination of water resources.

c) Attenuation of Pesticide Degradation Rate with Depth. There is a need to understand better the mechanisms of microbial degradation and to be able to predict likely degradation rates in relation to microbial populations.

d) Pesticide Transformations in Rivers. At present there is no great understanding of which processes control pesticide concentrations in rivers. Is there significant pesticide degradation? Are interactions with suspended sediments important? If suspended sediments settle on to the stream bed can they be released back into the water column? Are pesticides in river sediments bioavailable or toxic to stream biota?

e) Pesticide in Raw Water for Public Supply. Methods are required that can take estimates of pesticide run-off, at the edge of field or from headwater catchments, and translate them into pesticide concentrations further downstream where water may be extracted for public supply. Such predictions may allow water utilities to run advanced water treatment processes (eg activated carbon filters) more economically.

f) Integrated Catchment Management. There is a need to develop policies and methodologies that can be used to manage catchments as units, taking account of water quality within catchments and emitted from catchments.

g) Pesticide Impacts on Mammals. There are important gaps in European coverage on the effects of pesticides on mammals, not just in rural areas but also in urban areas. Of particular interest are small mammals (mice, voles shrews), squirrels, hedgehogs, bats and deer.

4 Pesticide groups and environmental problems

The following tables catogorize some commonly used pesticides by main group (eg herbicide) and then by chemical family. Potential environmental problems are highlighted.

Table 1 *Insecticides*

Pesticide Group	Examples	Potential Problems
Organochlorines	aldrin*, lindane, DDT*	Bioaccumulation. Acute toxicity. Reproductive Failure in Birds. Toxicity to Bats in Wood preservatives.
Organophosphorous	dichlorvos, fenitrothion, carbophenothion	Acute toxicity to some bird species. Toxic to bees. Some humans highly sensitive.
Carbamates	aldicarb, carbofuran, pirimicarb	Secondry poisoning of birds. Possible carcinogicity to man. Toxic to bees.
Dinitrophenols	DNOC*	Toxicity to man.
Pyrethroids	permethrin, cypermethrin, fenvalerate	Toxic to aquatic invertebrates and fish. Availability of bound residues to organisms.

Note: * - Now banned or restricted.

Table 2 *Herbicides*

Pesticide Group	Examples	Potential Problems
Phenoxyherbicides	2,4-D, MCPA, Mecoprop, Dichlorprop	Implicated in carcinogenic and tetrogenic problems from dioxin contamination of 2,4,5-T. Spray drift damage.
Ureas	Diuron, linuron, chlorosulphuron, bromacil	Damage to following crops. Implied contamination of ground water.
Triazines	atrazine, simazine, prometryn amitrole	Contamination of groundwater and surface waters.
Anilides	alachlor	A few of these are acutely toxic but are non-persistent.
Picolinics	picloram, clopyralid	
Thiocarbamates	di-allate, EPTC	Contamination of the environment is not known in most cases.
Nitriles	dichlorbenil	
Dinitroanalines	trifluralin, oryzalin	There are some problems in analyzing some of these chemicals at very low concentrations.
Amides	propachlor	
Bipyridyls	diquat; paraquat	
Nitrophenyl ethers	bifenox	
HBN	bromoxynil, ioxynil	
Benzoic acids	dicamba, chloramben	
Phosphonoglycines	glyphosphate	
Phosphonate	fosamine, fosetyl	
Pyridine	triclopyr	

Table 3 *Fungicides*

Pesticide Group	Examples	Potential Problems
Metal Containing	organotins*, inorganic mercury, organomercury, copper	Toxic to aquatic organisms. Formation of organometals in the environment and thence bioaccumulation and hazard to man.
Dithiocarbamates	maneb, zineb, ferbam, thiram	Possible human health problems.
Dicarboximide	capafol, captan	Possible human health effects
Chlorinated phenols	pentachlorophenol*	Toxic to bats in wood preservative.
MBC fungicides	benomyl, thiophanate-methyl	Human health problems suspected in some cases.
Phenylamide	bealaxyl, metalaxyl	
Oxathin	carboxin	Possible residues in food.
Oxazole	hymexazol, drazoxolon	
Imidazole	imazalil, prochloraz	
Dicarboximide		
Isothiazolone	octhilinone	
Thiazole	etridiazole	
Dinitrophenol	dinocap*	
Nitroanaline	dicloram	
Quinone	dithianon	
Morpholine	dodemorph, fenpropimorph	
Piperidine	fenpropidin	

Note: * - Now banned or restricted.

5 Sources of information

a) General news and articles

Pesticide News	-	published by The Pesticide Trust, Eurolink centre, 49 Effra Rd., London, SW2 1BZ, UK. Produced quarterly.
Pesticide Outlook	-	published by the Royal Society of Chemistry Information Service. Produced quarterly.

b) Reference Books

The UK Pesticide Guide	-	published by the British Crop Protection Council. Annual update. Profiles of pesticides under usage, efficacy, precautions for use, indexed by crops.
The Pesticide Manual	-	published by the British Crop Protection Council, 9th edition. Formulations, structures, some physico-chemical properties, toxicology, analytical methods.
The Agrochemicals Handbook	-	published by the Royal Society of Chemistry, 3rd edition, 6 monthly updates. Data similar to the Pesticide Manual.
The Dictionary of Substances and their Effects	-	published by Royal Society of Chemistry volumes not only first 3 available. Lists for 5000 chemicals, occupational exposure, legal status worldwide, uses, ecotoxicology, mammalian toxicology and physical properties.
The SCS/ARES/CES Pesticide - Properties Database for Environment Decision Making		Reviews of Environmental Contamination and Toxicology, Vol 23, Springer Verlag. Physico-chemical data on a wide range of pesticides. The range of measured values is assessed and single values recommended.

c) **Computer Databases (a small selection)**

TOXLINE - US national Institutes of Health, Bethesda, Maryland accessible online, very comprehensive.

IRPTC - UNEP database, Geneva Switzerland. Queries are sent to IRPTC headquarters who provide printouts. Covers, chemical structure, production methods, use and sources of environmental pollution, levels in the environment, toxicity to mammals, kinetics, environmental toxicity, degradation and environmental fate, legal file, disposal of waste.

ECDIN - Created under the Environmental Research Programme of the Joint Research Centre of the European Communities. Covers, physico-chemical properties, production and use, legislation and rules, occupational health and safety, toxicity, concentrations and fate in the environment, detection methods, hazards. Available on-line and as a CD-ROM.

Appendix 1 Fate and behaviour of pesticides in structured clay soils

FATE AND BEHAVIOUR OF PESTICIDES IN STRUCTURED CLAY SOILS

First Interim Report

by

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Contents

Executive Summary

This report presents results from the first year of a study of the hydrological and hydrochemical factors and processes that influence the fate and behaviour of pesticides in a clay catchment. The specific objectives of the project are to study pesticide mobility and degradation in relation to soil water dynamics, crop husbandry and climatic factors, and to develop and validate physically-based models of pesticide transport. The wider objectives of the project are to identify practical means of minimising the risk of pollution by pesticides and to develop strategies for monitoring pesticide pollution at the catchment scale.

Experimental studies involved instrumenting and monitoring a new field site on the Oxford University Farm at Wytham. The field selected for the study was underlain with a structured clay soil and planted with winter wheat. Equipment installed at the site included arrays of tensiometers, neutron probe access tubes, run-off traps and measuring devices, soil suction samplers, and a drain flow meter with autosampler. Soil water samples, soil columns and soil samples were collected in the field for analysis and chemical and microbiological experiments in the laboratory.

Drainflow was initiated in response to rainfall events 50 days after isoproturon application. Relatively high concentrations of pesticide, between 200 and 500 μg/l, were found in the drain water during those events, representing a 2.7% loss of available pesticide within 3 days. Other water samples taken manually during this major rain event period also contained high pesticide concentrations (800 μg/l in overland flow and 24 μg/l in the ditch). Drainflow was found to commence soon after the topsoil became saturated. The evidence suggested the drains being filled by water entering from above via macropores, both biopores and cracks. Peak pesticide concentrations in the drain water were interpreted as being related to the intensity of the preceding rainfall once the soil surface had become saturated. In addition differences between peak pesticide and anion concentrations in the drainwater suggested that the drainwater was composed of both water emanating from the surface and from within the profile.

Evidence for lateral interflow was obtained using a bromide tracer. Overall water movement in the field moved via lateral routes; overland flow, lateral interflow and via mole drainflow with interconnections being made by macropores. The high pesticide loss to drainage revealed in this report underlines the potential for surface water contamination in mole drained clay soils. This potential remains even after a considerable time has lapsed since application.

At the time of preparation of this report, a second field season of experiments has started at the Wytham site. The main aims of this second season are to verify the main findings of the first season and to obtain more data on the partitioning both of water movement and pesticide between overland, interflow and drainflow.

Funding has come from a number of sources which include a project funded by the Natural Environment Research Council (NERC) and a project funded jointly by the NERC and the Agriculture and Food Research Council. This second project is being conducted in collaboration with the Soil Survey and Land Resources Centre and Horticulture Research International.

1. Introduction

A number of drinking water sources, both ground and surface waters, in England and Wales have been shown to be contaminated with pesticides (Lees and McVeigh, 1988; Drinking Water Inspectorate, 1992). In many cases levels of individual pesticides are above the maximum acceptable concentration of 0.1 μg/l laid down in the European Community Drinking Water Directive (Council of the European Communities Directive, 1980). In the case of some pesticides contamination may be caused by non agricultural use (Gomme *et al*, 1992). However, two studies of small agricultural clay catchments in England have shown a direct link between agricultural usage and pesticide runoff (Matthiessen *et al.*, 1992, Williams *et al.*, 1991, Harris *et al.*, 1991). The movement of pesticides from agricultural clay catchments is of particular interest, as they account for 45% of the cereal growing area of England and Wales (Cannel *et al.*, 1984). The low matrix conductivity of clay soils should mean that pesticide movement though the soil profile is very slow, thus representing little risk of pollution of water courses. However, as has been stated above, significant losses of pesticides to drainage water have been reported from clay catchments. The processes by which pesticides can be transported from clay soils are therefore of particular scientific and environmental importance.

The hydrology of clay soils is strongly influenced by the presence of macropores consisting of both biopores, created by worm activity, and mechanical fissures resulting from shrink swell processes (Kneale, 1986). The presence of macropores allows the rapid movement of water through the profile, by-passing various amounts of the soil matrix (Kneale and White, 1984, Leeds-Harrison *et al.*, 1986). Clay soils are often drained by a combination of mole and tile drains so as to reduce seasonal water-logging. The drains are designed to intercept lateral flow in the upper horizons; this lateral flow is likely to be augmented by macropore flow both horizontally and vertically. Thus subsurface flow routes will exist for water that may be moving at velocities close to that of overland flow (Bevan and German, 1982), resulting in a rapid movement of water and dissolved solutes to surface waters.

The rapid movement of nitrogen from the upper soil profile, caused by the mineralization of organic-N, observed at Wytham Farm, Oxford during autumn, has been attributed to the action of macropores creating by-pass flow (White *et al*, 1983). A similar flushing effect has been observed following the application of pesticides at ADAS Rosemaund Experimental Husbandry Farm (Mattheissen *et al.*, 1992. Williams *et al.*, 1991). Although the percentage of pesticide lost by this route was only $< 1\%$ of that applied, observed concentrations in drains and the receiving stream were often in excess of 10 μg/l, exceeding the current maximum acceptable concentration in drinking water by two orders of magnitude.

It is clear that solutes and in particular pesticides are able to by-pass the soil profile to contaminate surface waters, however, the factors controlling the magnitude of observed concentrations in clay soils are still unclear. In principle the physico-chemical properties of the pesticide are the key to determining its level and persistence in the environment. For example a highly sorbed, rapidly degraded chemical would not be expected, in the normal course of events, to appear in surface or groundwaters. This kind of generalized statement is reasonable for soils in which water flow is through the soil matrix, where there is good contact between soil and water. The nature of by-pass flow is to remove the intimate contact between soil and water thus reducing the possibilities for both sorption and degradation. The extent of the interaction between matric and macropore water, and the hydrological conditions

of the soil by which this is controlled are key to understanding, and therefore predicting pesticide transport through structured clay soils.

A detailed hydrological and chemical process study has been set up at Wytham Farm, Oxford, to identify the *in situ* processes of water transport over, within and below the soil in relation to rainfall, antecedent water conditions and agricultural practice. This will provide the information for creating physically-based conceptual models, which should represent realistically the actual conditions of water inputs through various pathways to the outflow from agricultural catchments. The combination of this information with parallel chemical and microbiological studies will make it possible to determine the potential transport of agrochemicals in solution to aquifers and surface waters.

Some of the results given in this report were presented previously as part of a joint report with Alan Walker (HRI) and Andrée Carter (SSLRC) to the Special Topic Steering Committee.

2. Experimental site

2.1 LOCATION AND DESCRIPTION

The clay catchment chosen for this study, located at Oxford University Farm, Wytham in Oxfordshire, is shown in Figure 1. This catchment has previously been used in hydrological studies, such as those conducted by Kneale (1986), and Haigh (1985). It should be noted that Wytham Farm is also being used as the location of studies for the Environmental Change Network (ECN).

The design of the experiments used at Wytham have been based on experience gained at three field process studies that were carried out at ADAS Rosemaund EHF during 1989-1993, (Bell *et al.*, 1991; Williams *et al.*, 1991; Bell *et al.*, 1992). Although the studies at Rosemaund obtained much useful and original information on the hydrological processes that influence pesticide transport, it was clear that a more comprehensive approach was required. The experiments at Wytham and in the laboratories at IH are designed to combine, the hydrological, hydrochemical and microbiological studies information, to provide a clearer picture of the processes which lead to pesticide transport.

The experimental area was on a structured clay soil under arable cultivation of winter wheat that had been moled and ploughed in August, 1992. The ploughing had incorporated the straw and stubble, forming a "buried straw horizon" at a depth ranging from about 0.15 to 0.2 m. The instruments were installed over an area of approximately 25 m by 50 m between field drains 2 and 3 midway up the field. The moles were installed at 3 m intervals, and at a depth of 0.5 m, and drain into the backfill of the field drains, situated 0.75 m below the soil surface (see Figure 2). The site slopes towards the drainage ditch at a gradient of approximately 1:20. The soil within the plot was classified by an SSLRC soil survey to belong to the Denchworth series (Jarvis and Hazelden, 1982). Field instrumentation is described in later sections and a schematic diagram of the Wytham site is shown in Figure 2.

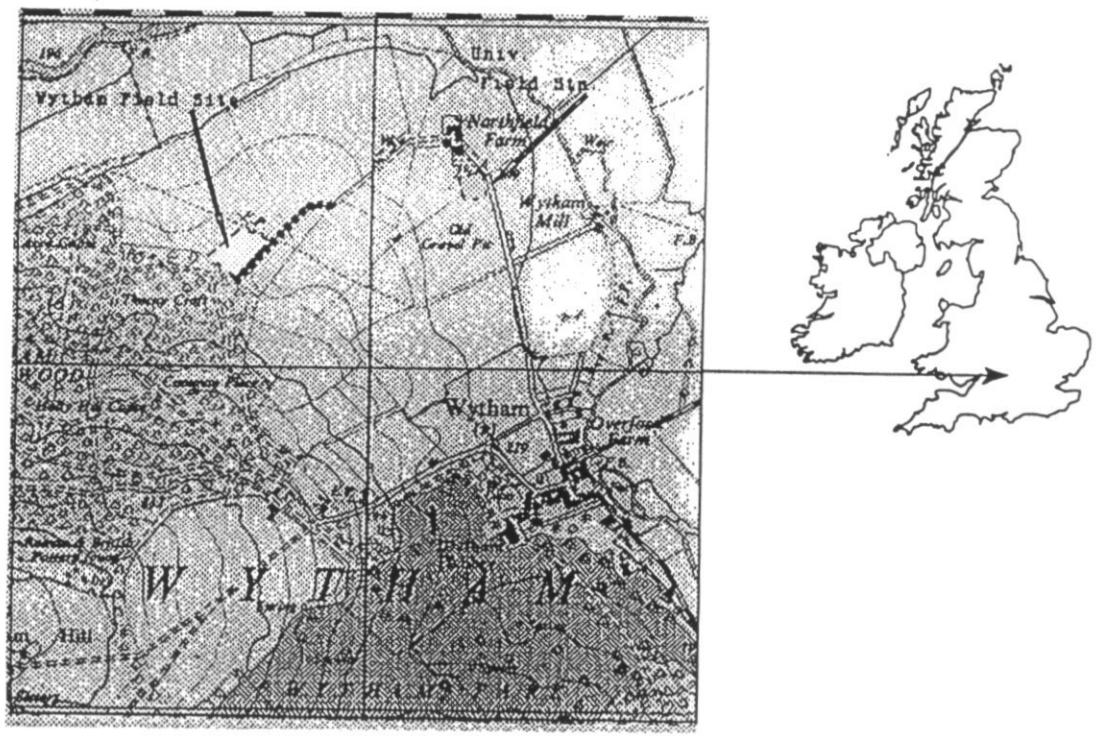

Figure 1. Location of the field site at Wytham

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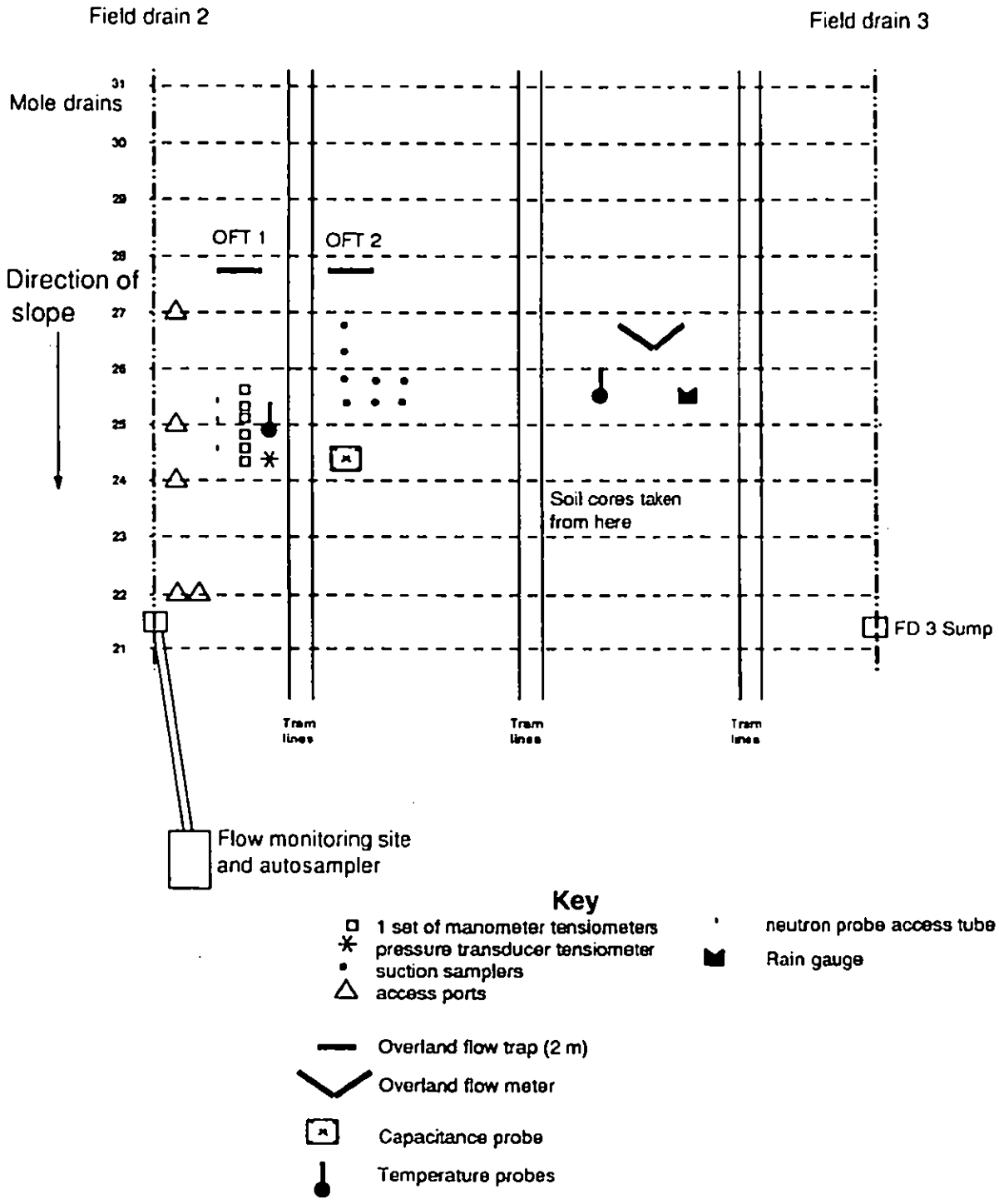


Figure 2. Location of instruments at Wytham for 1992-93 season (superimposed over drain locations)

The initial installation and set-up of the field site proved to be considerably more demanding than had been anticipated, mainly due to the difficulties of working in a waterlogged heavy clay soil during a wet autumn/winter. Rainfall during the winter months was higher than average in December 1992, and in January 1993 was almost double the long term mean monthly rainfall (Figure 8).

2.2 SOIL TYPE

The main profile characteristics of the Denchworth series are a dark brown clayey Apg horizon with a well developed subangular blocky structure. The underlying olive clayey Bg horizon has a strongly developed coarse angular blocky structure. Previous studies report a clay content of approximately 30-40% in the top 30 cm and 60-70% from 40-80 cm, with a bulk density of 1.6 in the upper horizon compared to 1.8-1.9 in the lower horizon. Profiles are very slightly porous and slowly permeable in the subsoil.

The soil is often waterlogged for long periods over the winter, but in dry conditions deep cracks develop which may help to drain autumn rainfall. A closely spaced (20 m) system of pipes supplemented by mole drains is recommended for drainage.

The Total Organic Carbon (TOC) of the top soil and the lower 'B' horizon were analysed to reveal 2.57% in the top soil and 0.48% in the lower horizon, a five fold difference. The dominant clay minerals in the top soil were kaolinite and illite, and in the lower horizon were kaolinite, illite and smectite (see Figure 6). CEC values for the soil series have been given in the range of 35-48 meq/100g (Jarvis and Hazelden, 1982). The combination of a high clay content, with high CEC and a relatively high organic carbon content would suggest that the soil at Wytham would have a relatively high adsorptive capacity for organic compounds.

This soil association covers approximately 1.86% of the total land area of England and Wales but soils with similar hydrology account for 4.95% (including Scotland). Heavy clay soils such as Denchworth series have a tendency to crack and exhibit by-pass flow, and are thought to represent 33% of the land area of England and Wales.

2.3 CROP HUSBANDRY

A winter wheat crop was harvested in August, leaving both stubble and chopped straw on the soil surface. The field was then mole drained. The beam mole plough comprised of a blade leading down to a 3" bullet which was connected to a following ball and chain. The mole depth was approximately 50 cm and the mole drains were at 3 m intervals. The field was then cultivated by ploughing to 15-20 cm. The field was cultivated using a 'Roterra' (powered harrow) and then drilled with winter wheat (variety Haven). Tram lines were set at 12 m intervals. Draza slug pellets (Bayer, active ingredient 4% methiocarb) were applied at 5.5 kg/ha on 11,10,92.

Isoproturon was the active ingredient at 2.5 kg/ha in Javelin Gold (Rhone Poulenc) applied to the field on 10,2,93 to control blackgrass. Nitrate was applied on 6,3,93 in the form of urea (46% N) at a rate of 125 kg/ha. On 15,4,93 the pesticide 'Cheetah' (Hoechst, active ingredient fenoxaprop-ethyl, 60g/l) was applied to control black grass at 2 l/ha in conjunction with 1.5 l/ha Cycocel (a growth regulator) and 1 l/ha LI 700 (adjuvant). On 26,4,93 a further 281 Kg/ha urea was applied to the field. On 30,4,93 0.6 l/ha Starane was applied

(Dow Elenco, active ingredient 200 g/l fluoroxypyr) to control Cleavers and 0.8 l/ha Sportak (Schering) was used as a fungicide. On 18,5,93 1.5 l/ha Cheetah and 1 l/ha Li 700 were again applied to the field. On 21,6,93 1.5 l/ha Impact Excell and 0.5 l/ha Mistral fungicides were applied to the field.

The crop was harvested in mid August, 1993 and the straw baled. The plot was ploughed to a depth of 15-20 cm. On 18,10,93 the plot was cultivated with a 'Roterra' and on the 20,10,93 the field was sown with winter barley, variety Fighter.

2.4 TIMETABLE OF EVENTS

8,92	Winter wheat crop harvested
	Mole drains put in by beam mole plough
	Ploughing and cultivation with powered harrow
9,92	Drilling with winter wheat
11,10,92	Slug pellet application
	Installation of experimental equipment
12,92	Installation completed
10,2,93	Isoproturon applied to control blackgrass
6,3,93	N-fertiliser applied
1,4,93	Significant rainfall and drainflow
12,4,93	No more significant drainflow
15,4,93	Fenoxaprop-ethyl applied to control blackgrass
26,4,93	N-fertiliser applied
22,7,93	Last water samples collected
	Experimental equipment removed
8,93	Crop harvested

3. Methods

3.1 FIELD EXPERIMENTATION

3.1.1 Soil hydrology

The 1992/93 experimental programme comprised of three components:

Monitoring of surface hydrology to determine hydrological inputs and processes.
Rainfall was monitored using tipping bucket rain gauges connected to loggers (Campbell Scientific, USA); effects on surface hydrology being assessed by logging pressure transducer tensiometers (PTTs) and a capacitance probe (Institute of Hydrology, UK) at 10cm depth. Overland flow was collected and measured using guttering lined with damp-proof sheeting inserted into the soil 0.05 m below the surface. Slotted Osma drain and gravel was placed in the gutter, and the whole installation was roofed to prevent the direct entry of rainfall. This was installed in the form of a 4 x 4m 'V', with the 'V' facing upslope. The water collected in the guttering was led to a tipping bucket raingauge by a 8.2 cm drainpipe, the tips being

recorded by a Campbell logger.

Monitoring the influence of rainfall and drainage on the status of the soil water reservoir and related soil water dynamics.
A set of 30 manual mercury manometer tensiometers which straddled mole drain 25 (see Figure 2) were installed at depths of 0.1, 0.3, 0.5, 0.75, and 1.0 m, to give 2-dimensional profiles of potentials around the mole drain. The 0.5 - 1.0 m manual tensiometers were inserted through access tubes and were angled so the profile of porous cups at the different depths were vertically in line. The angled insertion of tensiometers was to reduce the effects of lateral spatial variability. Five pressure transducer tensiometers (PTT) were installed at the same depths at a position 1.5 m from the manual tensiometers. In front of the manual tensiometers 3 neutron probe access tubes were installed to a depth of 1.5 m to enable the employment of a neutron probe (Didcot Instruments, UK), to measure volumetric water contents at 0.1 m increments from the soil surface.

Monitoring the flow of water in field drain 2
Field drain 2 was intercepted at a point equidistant between moles 22 and 21 and the drainage water was fed by an 80 mm pipe to a v-notch weir at the soil surface, some 15 m downslope of the interception point. Pressure transducers were used to determine the height of water in the weir, and by use of a calibration equation the flow rate was deduced.

Monitoring of soil water status commenced in November 1992 and continued throughout the crop cycle.

3.1.2 Soil and water sampling

Suction samplers were installed at three depths (0.25, 0.5 and 0.75 m) through aluminium access tubes to assess isoproturon concentrations in the soil pore water. The augured hole was partially filled with silica flour into which the ceramic pots of the suction samplers were bedded. Two overland flow traps (2 m in length) supplied by SSLRC were installed and connected to 5 l plastic sampling vessels. At the field drain 2 v-notch weir flow gauge site an automatic sampling device was installed (triggered by the height of water collected in the weir box it fills twenty-four 1 l bottles). The 'catchment' of this tile drain prior to its interception was estimated to be 1800 m^2.

Access tubes (110 mm) were positioned directly over mole drains 25, 24 and 22 and small glass beakers (75 ml) installed in the bottom of the moles to act as sumps for water sampling (Figure 2.).

On the same day as pesticide application 1 l of 10000 ppm KBr was applied via a watering can to a 0.5 m^2 area 1.5 m upslope of the 0.25 m suction samplers, and also over the position of mole drain 25, 2 m away from the intersection with field drain 2.

In addition, filter paper discs (Whatman no. 1, 10 cm dia.) were placed across the plot (fastened on wooden battens to keep above the moist soil) to collect the pesticide spray and estimate the true application rate of the pesticide.

Throughout the season water samples were taken manually from the field drain 2 outflow and ditch at the bottom of the field.

As soil coring techniques proved difficult to use due to the sticky consistency of the soil, soil was collected only from the upper 2 cm of the soil with a spatula. At fortnightly intervals 1 kg amounts of soil were collected from 1 m^2 plots, which were sampled in sequence from one end of the experimental plot to the other. Samples were frozen prior to analysis.

3.2 LABORATORY ANALYSIS AND EXPERIMENTATION

3.2.1 Sample preparation, concentration and analysis

Water samples were maintained at 4°C prior to analysis (not more than 1 month). Prior to isoproturon analysis samples were first concentrated using C18 bond elute cartridges (Sorbex) and eluted from the column with a solution of 100% methanol. Analysis of isoproturon was by hplc with a C8 column and acetonitrile/water eluent with detection at 240 nm.

Prior to anion analysis a 5 ml aliquot was taken from the original water sample and filtered using 0.45 um disposable filters (Millipore). Samples were analysed using a Dionex ion chromatograph. The eluent used contained 1.8 mM sodium bicarbonate and 1.7 mM sodium carbonate. The regenerant used was 25 mM sulphuric acid. Detection was by electrical conductivity.

Soil samples were analysed for isoproturon by taking four 30 g samples and extracting with 50 ml methanol prior to determination by hplc.

3.2.2 Total organic carbon analysis

From soil collected from the topsoil and 40 cm, 4 replicate sub-samples of 2 g were placed in small porcelain crucibles. A solution of 4M HCl containing 30 g/l $FeCl_2.4H_2O$ (to prevent any MnO_2 present from indirectly oxidising the organic carbon) was used to saturate the soil in the crucibles to remove carbonates. The crucibles were placed on a hot plate in a fume cupboard for 2 days to evaporate off the solution. The dried soil samples were then weighed accurately in 0.2 g amounts on terracotta crucibles and then analysed with a LECO 444 carbon/sulphur analyser with a furnace temperature of 1400°C.

3.2.3 Clay mineralogy

Soil samples were taken from a soil pit from the top 5 cm and 40 cm depths for analysis. In addition sediment found in tile drain water collected during a rain storm in December was filtered prior to semi-quantitative clay mineral analysis. The equipment used comprised a B-pex goniometer with an EFG X-ray generator.

3.2.4 Total aerobic heterotrophic bacteria

From topsoil and 40 cm soil collected from a soil pit a 1 g sub-sample was placed in a sterile Universal bottle containing 9 ml quarter strength ringer solution (3 replicates). After shaking the sample was diluted 10,000 times in further bottles of sterile ringers solution before plating out using 0.05 ml drops from disposable sterile pastettes onto 0.3% Tryptone Soya Agar (Oxoid) (0.5% agar). The plates were incubated at 20°C for 2 days prior to counting.

3.2.5 Degradation of ^{14}C-labelled isoproturon

Subsamples of topsoil and 40 cm soil samples collected from a soil pit were used to measure moisture content through weight loss after incubation at 105°C overnight. The soil samples were air dried for 2 days so that the samples had lost 10% of their original moisture content. The samples were then ground with a sterile pestle and mortar (flamed in ethanol) and 3 mm sieved. The soils were then placed in 150 ml conical Quickfit flasks and weighed (6 replicates). ^{14}C-ring labelled isoproturon in a 10 mM $CaCl_2$ solution was added to the soil samples to a final concentration of 0.01 μg/g with a disposable pastette. The soils were returned to their original moisture content through the addition of further sterile 10 mM $CaCl_2$; this was 31.5% for the top soil and 21.6% for the 40 cm soil. The Quickfit conical flasks were connected via neoprene tubes to a pump which ran air through a CO_2 trap of soda lime before bubbling through water in a Drechsel flask prior to its introduction to the soil samples. Air from the conical flasks was then bubbled through a CO_2 trapping solution of 70 ml of 50 mM NaOH.

4. Results and discussion

4.1 WEATHER

A major factor influencing the processes of pesticide persistence and transport is the effect of the climate. The two most important factors are rainfall and temperature.

Rainfall data for the 1992/93 crop season is presented in Figure 8, and 10 and temperature data in Figure 11. Figure 8 shows the mean monthly rainfall at Wytham compared with the long term monthly means. December 1992 had slightly above average rainfall, however January 1993 produced almost twice the average monthly rainfall. This created very wet, waterlogged, conditions; and delayed the spraying of pesticide until 10 February 1993.

February and March 1993 proved to be much drier than average, such that desiccation cracks of 2-4 cm depth could be observed at the soil surface. The little rain that did fall over this period produced no significant drainflow events. The first major storm, occurred on 1 April, 1993, and produced the first significant drainflow and pesticide transport. Rainfall between the period of 1-12 April generated a series of drainflow events. No more significant drainflow events occurred after this period.

Temperature data for the 1992/93 crop season (Figure 11) shows the mean daily temperature values after spraying. From the end of April shrinkage cracks were increasingly apparent. Drier conditions in the topsoil is a factor known to reduce microbial activity. Thus, the pesticide may persist for longer than under wetter conditions, but in the absence of transport to the drains it no longer represents an immediate contamination threat to surrounding water courses.

4.2 SOIL STRUCTURE AND HYDROLOGY

4.2.1. Soil profile and physical characteristics

Results presented cover the data assimilated over the initial five/six months from the end of November 1992 to mid July, 1993.

Manometer tensiometer data were analysed to produce 2-D distributions of soil water potentials. These showed the spatial temporal wetting and drying around mole drain 25 during the crop cycle. Data showing total soil water potentials around a mole drain during saturated field conditions in the winter months is presented in Figure 3. Ranges of total soil water potential were represented by different letters defined within the key. Saturation in Figure 3 was shown as the area above the solid line.

The presence of a saturated zone at 0.3-0.4 m up to the soil surface, resulting from a build up of saturation above a lower horizon of low hydraulic conductivity, was clearly indicated and the evidence was corroborated by pressure transducer tensiometer (PTT) data in Figure 4. Figure 4 showed conditions greater than saturation (ie. a positive head of water) at the soil surface, during and after the storm event on 6/7th December 1992. This was shown by the potential at 0.1 m being greater than -1 kpa, and at 0.3 m greater than -3 kpa.

No evidence of a permanent water table under these wet conditions within the top 1.0 m was seen from the tensiometer data shown in Figures 3 and 4 as total soil water potentials never became greater than -10 kpa during this period.

Data presented by Jarvis & Hazelden (1982) indicated that downward movement of water in the Denchworth series was likely to be severely restricted below the topsoil. An increase in clay content from 38% to 73% between 0.3 m and 0.4 m and a corresponding increase in packing density from 1.6 to 1.9 gcm-3 can be expected. This would present a significant barrier to vertical infiltration within the profile. This boundary (providing the base for the saturated zone) at about 0.35 m corresponds well with changes in soil type and can be attributed to the change from A to B horizons within the profile at Wytham. Another boundary change was seen at a depth of 0.8 m which was indicated by the presence of a wetter zone above 0.8 m than below that depth, shown in Figure 5, from data collected from the manual tensiometers. The profile from 0.35-0.8 m seemed to consist of a higher fine clay content and greater bulk density, and consequently a much lower hydraulic conductivity than the rest of the profile. This can give rise to a secondary saturated zone at this lower depth. The low hydraulic conductivity (K) of the matrix (0.007-0.071 m/day at 0.6 m), associated with the Denchworth series, (Jarvis and Hazelden, 1982) and the presence of macropores suggest that preferential flow mechanisms would be dominant in this soil.

Another feature within the profile is the buried straw layer (at approximately 15 cm depth) resulting from the incorporation of the previous year's straw and stubble. This layer may influence hydrological processes such as lateral interflow and in addition may be a site of increased pesticide sorption.

One of the most important characteristics of this site is its significant shrink/swell capacity. The porosity of this site in terms of hydrology, in the winter months, is almost exclusively governed by biopores consisting of worm and old root channels. During the late spring and summer, extensive soil shrinkage fractures were observed, some extending to well below

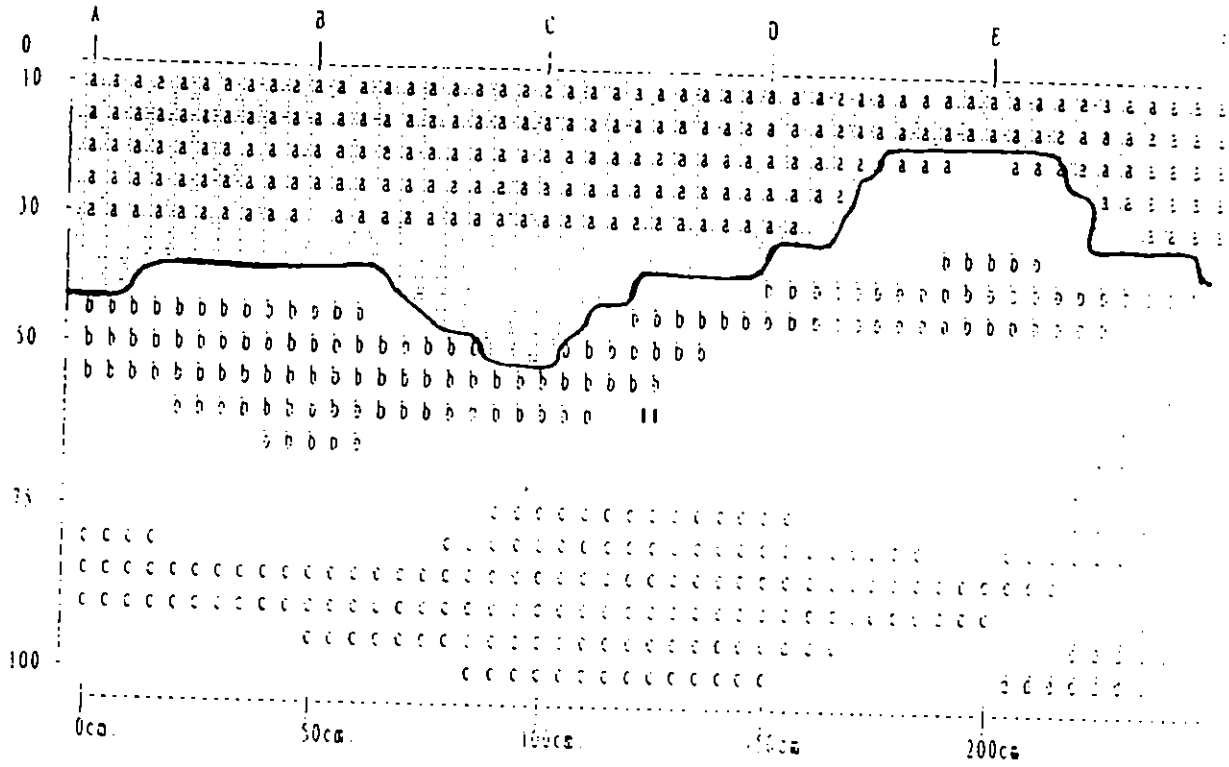


Fig. 3. Total potentials at 10-100 cm depths measured across mole drain 25 by manual tensiometers on 7,12,92

a:ptdest

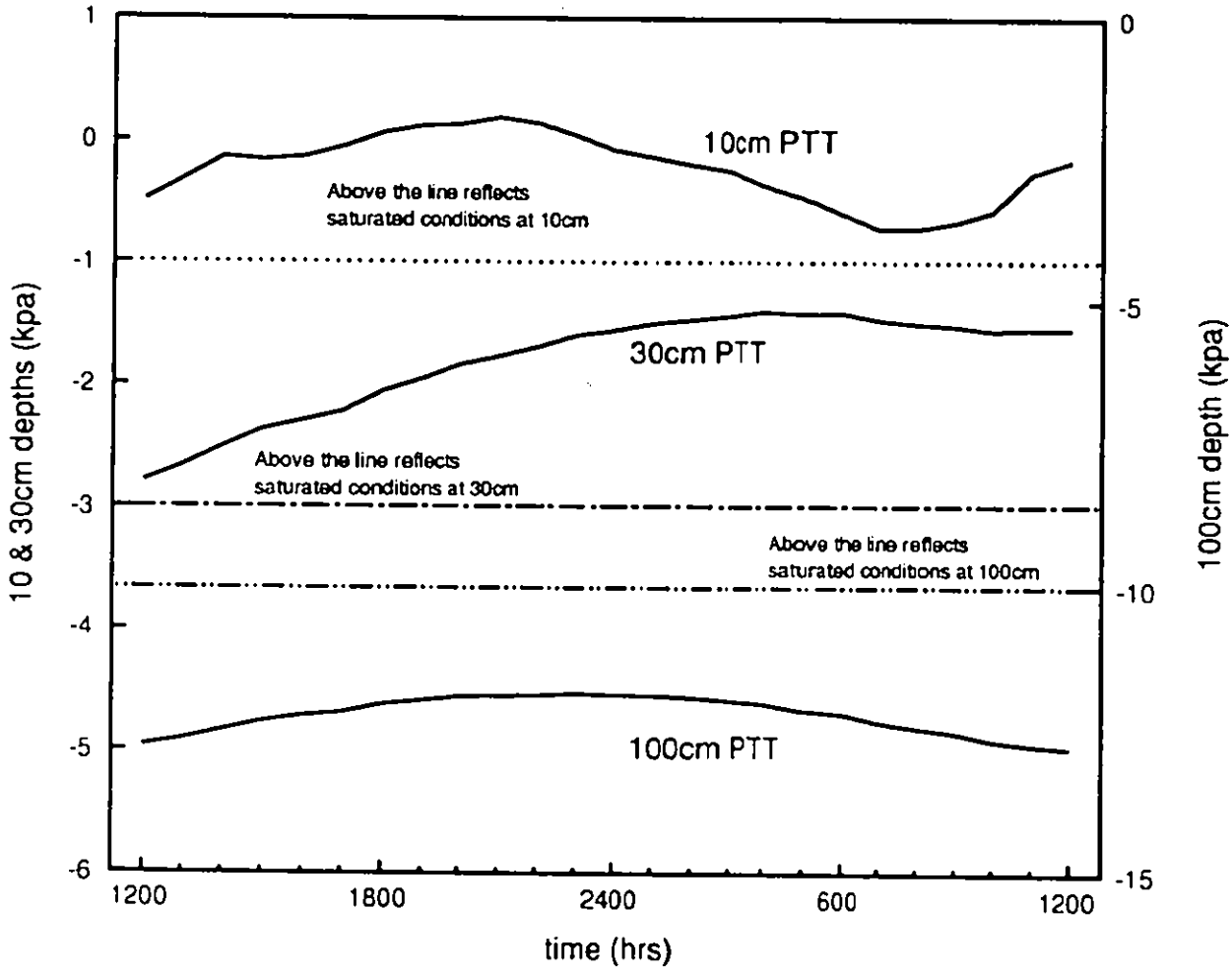
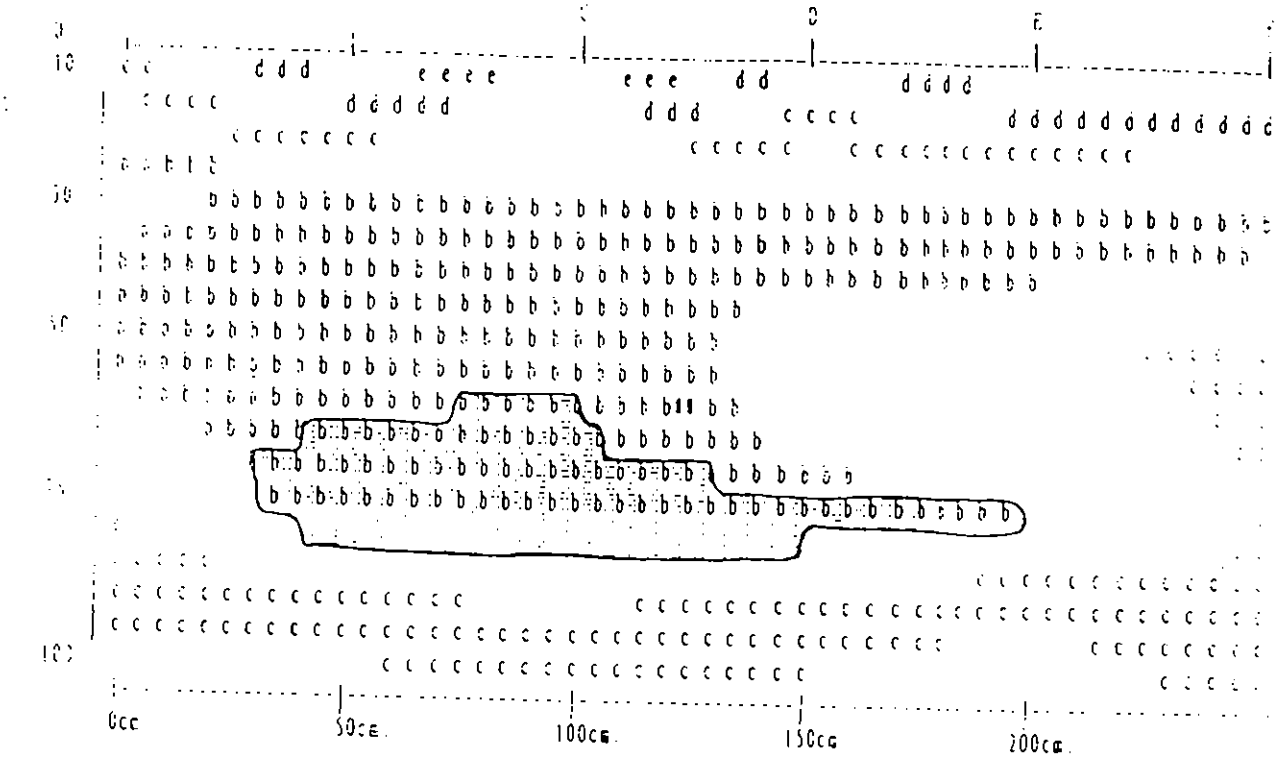


Figure 4. Total potentials at 10, 30 and 100 cm depths during rainfall event of 6th/7th December 1992



= SATURATED

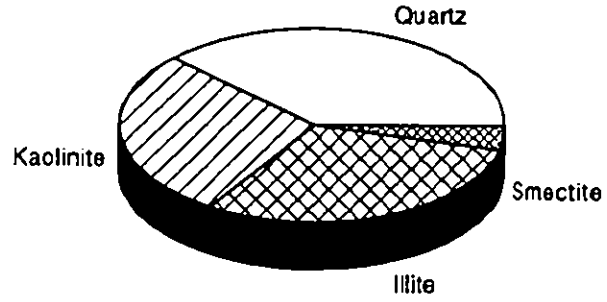
a = 0 to -2.5 kPa
b = -5.0 to -7.5 kPa
c = -10.0 to -12.5 kPa
d = -15.0 to -17.5 kPa
e = -20.0 to -22.5 kPa

= ESTIMATED DRAIN POSITION

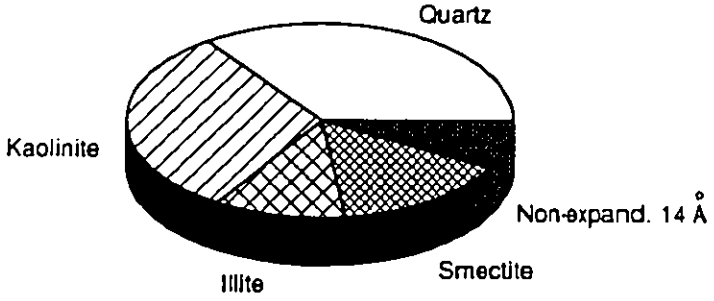
% OF CROSS SECTION ABOVE 30cm. WHICH IS SATURATED = 0.0 %
% OF CROSS SECTION ABOVE 50cm. WHICH IS SATURATED = 0.0 %
% OF TOTAL CROSS SECTION WHICH IS SATURATED = 9.5 %

Figure 5. Total potentials at 10-100 cm depths measured across mole drain 25 by manual tensiometers on 4,5,93.

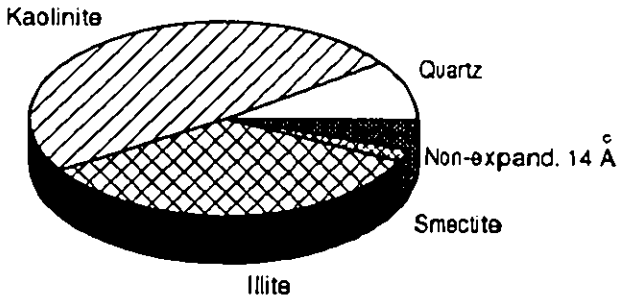
Claywy3



Soil surface



'B' horizon



Sediment found in field drain 2
from rainfall event 3,12,92

Figure 6. Clay mineralogy at Wytham

1m in depth at the height of the summer. As explained in the following section the water fluxes within the profile are determined by these macropores, both biological and physical in nature.

4.2.2. Observed flow pathways and antecedent conditions

Flow pathways were studied largely from data collected from a variety of instruments from a series of discete drainflow events. Data for the capacitance probe is not presented due to problems with calibration. This was possibly due to a 'salinity effect' whereby ions effect the frequency readings presented by the probe. Therefore, the relationship between frequency and water content is difficult to establish. Readings with the neutron probe were taken only in the latter part of the project, after April, 1993.

Storm event 1 (SE1) - 6/7th December 1992, 65 days before spray day.

Figure 7 describes SE 1 and shows the relationship between rainfall, overland flow (surface runoff), and drain flow from the field drain. Under surface saturated field conditions recorded rainfall events showed an immediate reaction in terms of drainflow. Due to this rapid response, and the absence of a water table/wetting front at mole drain depth, the drain flow events have been attributed to macropores providing water for the drains from the soil surface. This is in contrast to the more normal situation of the water table in periods of field capacity falling to a level controlled by the depth of the mole drains.

Studies have shown that macropore flow is the predominant process in the heavy clay soil at Wytham (Kneale and White, 1984; Kneale, 1986) and in other heavy clay soils (Beven and Germann, 1982; Bouma *et al.*, 1981). By-pass flow has been shown to occur in the noncapillary interpedal pore space whenever application rate exceeded the infiltration rate of the individual microaggregates (Radulovich *et al.*, 1992). At Wytham during the winter to early spring period by-pass flow was thought to be through macropore channels consisting of earthworm burrows and also most probably moling fissures, unlike the late spring and summer months which were dominated by shrinkage cracks. This is because during the winter cracks were not observed at the soil surface, however large numbers of open worm burrows were apparent at the surface.

Overland flow is thought to be produced by rainfall excess which occurs at the ground surface when the rainfall intensity exceeds the infiltration capacity (Pilgrim *et al.*, 1978). This is demonstrated clearly in Figure 7 where significant overland flow occurred 2 hours (approx.) after the start of rainfall. At this point one can assume that the macropores were working at maximum capacity, and unable to accept more water. The start of overland flow coincided with peak drain flow. It is important to note that significant overland flow, or sheet flow, is chronologically the secondary factor in the removal of excess precipitation. If the macropore infiltration capacity has not been reached then significant overland flow will not begin. During this storm event the volumes of overland flow were beyond the recording capability of the tipping bucket flow meter.

Unfortunately the drain flow measurement method in December, 1992 was artificially restrictive to flow and as a result the peak drain flow, as demonstrated by the plateau in Figure 7, is artificial. Therefore the percentage rainfall exiting as drain flow given in Table 1 for SE 1 is an underestimate. For SE 1 the water flow from the field drain to the V-notch weir was along a pipe whose internal diameter proved to be the dominant restrictive factor

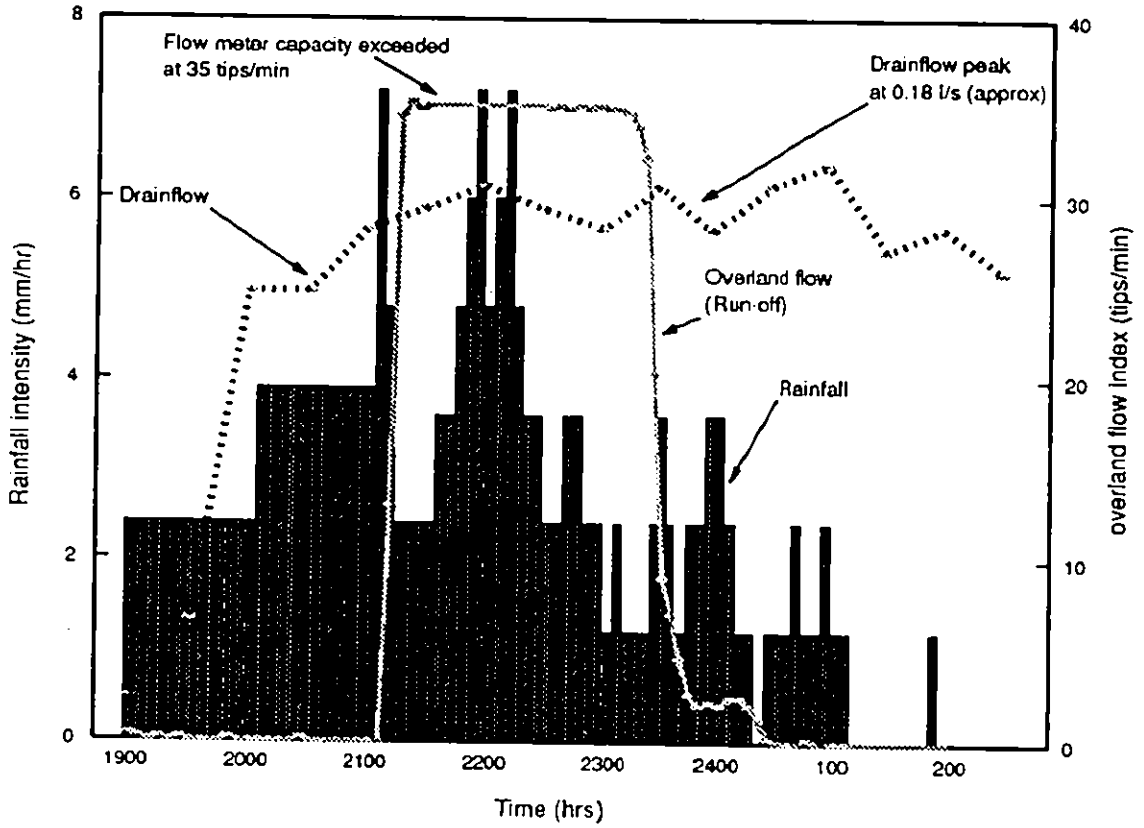


Figure 7. A comparison of rainfall, overland flow and drainflow at Wytham
6th/7th December 1992

to flow. This pipe was replaced with one whose internal diameter was equal to that of the field drain in late December, 1992. The presence of a saturated zone at 0.3-0.4 m depth immediately after SE 1 shown in Figure 3 suggests sub-surface lateral flow was also a feature during and after the storm event.

The clay mineral composition of sediment found in the field drain water is shown in Figure 6. Whilst it is difficult to ascertain the origin in the soil profile of all the sediment collected, the presence of a non-expandable 14 Å fraction suggested that some of the sediments had originated from the B horizon because the non-expandable 14 Å fraction did not occur in the other horizons.

Observed changes in conditions between December, 1992 and April, 1993

The topsoil remained close to saturation until early February 1993, at which time the absence of rainfall and the still conditions allowed the farmer onto the field to apply the pesticide. The period between the spraying of pesticide on 10/02/93 (day 0) and SE 2 on 01/04/93 (day 50), the first recorded significant drainflow event, was relatively dry as shown by data for February and March 1993 (Figure 8). The rainfall events that did occur at this time seem to have been sufficient to raise the matric potential at 10 cm to saturation, but for only brief periods (Figure 9), but ceased before any significant drain flow events were initiated. Rainfall and temperature data collected from 1 April, 1993 onwards are shown in Figures 10 and 11.

Storm event 2 (SE 2) - 1st April 1993, 50 days after spray day.

Figure 12 represents SE 2 which was the first recorded incidence of significant drainflow since spraying on 10th February 1993. The drainflow associated with that rainfall event has been plotted, along with the concentration of isoproturon present in water samples collected every 30 minutes by the triggered autosampler.

Overland flow was not picked up by the overland flow meter, however this equipment was believed to be out of commission during the April period. Water was collected in the overland flow traps (Figure 13); however the amount of overland flow could not be quantified.

The delay between the initiation of drainflow and rainfall was related to the drying of the topsoil that occurred from 10th February 1993 resulting in an increased soil water deficit (SWD) in the surface layer (0-0.05 m). Shallow cracks during this period were clearly visible at the soil surface. The rainfall that fell before the start of drain flow was assumed to be used to satisfy this SWD, although the entire deficit within the profile down to drain depth was not reduced to zero before drain flow occurred. This is demonstrated in Figure 14 where PTT data showed the surface 10 cm to have a positive head of water, and the soil at 30 cm to be unsaturated, when the field drain was flowing during SE 2.

Robinson *et al.* (1987) also showed 42% of storm rainfall passing through mole drains despite the soil moisture content being well below "field capacity". Although the soil profile was not completely saturated, the major pathways, ie. macropores, had to be surrounded by soil at a soil water content which was conducive to those pathways functioning. This would also include the soil surface as a major pathway of water supply to macropores (Beven and Germann, 1982).

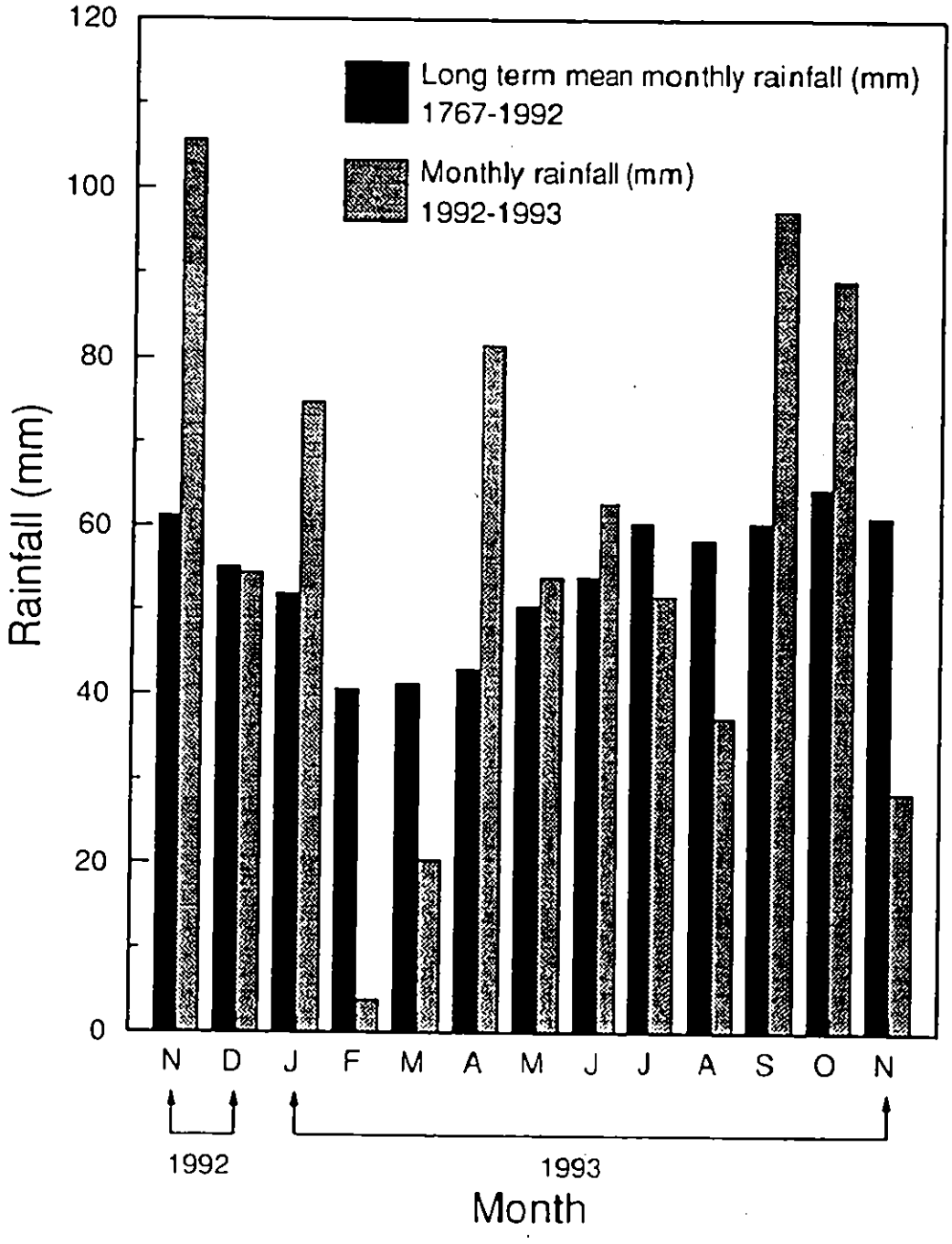


Figure 8. Comparison of long term mean monthly rainfall with monthly rainfall in 1992/3

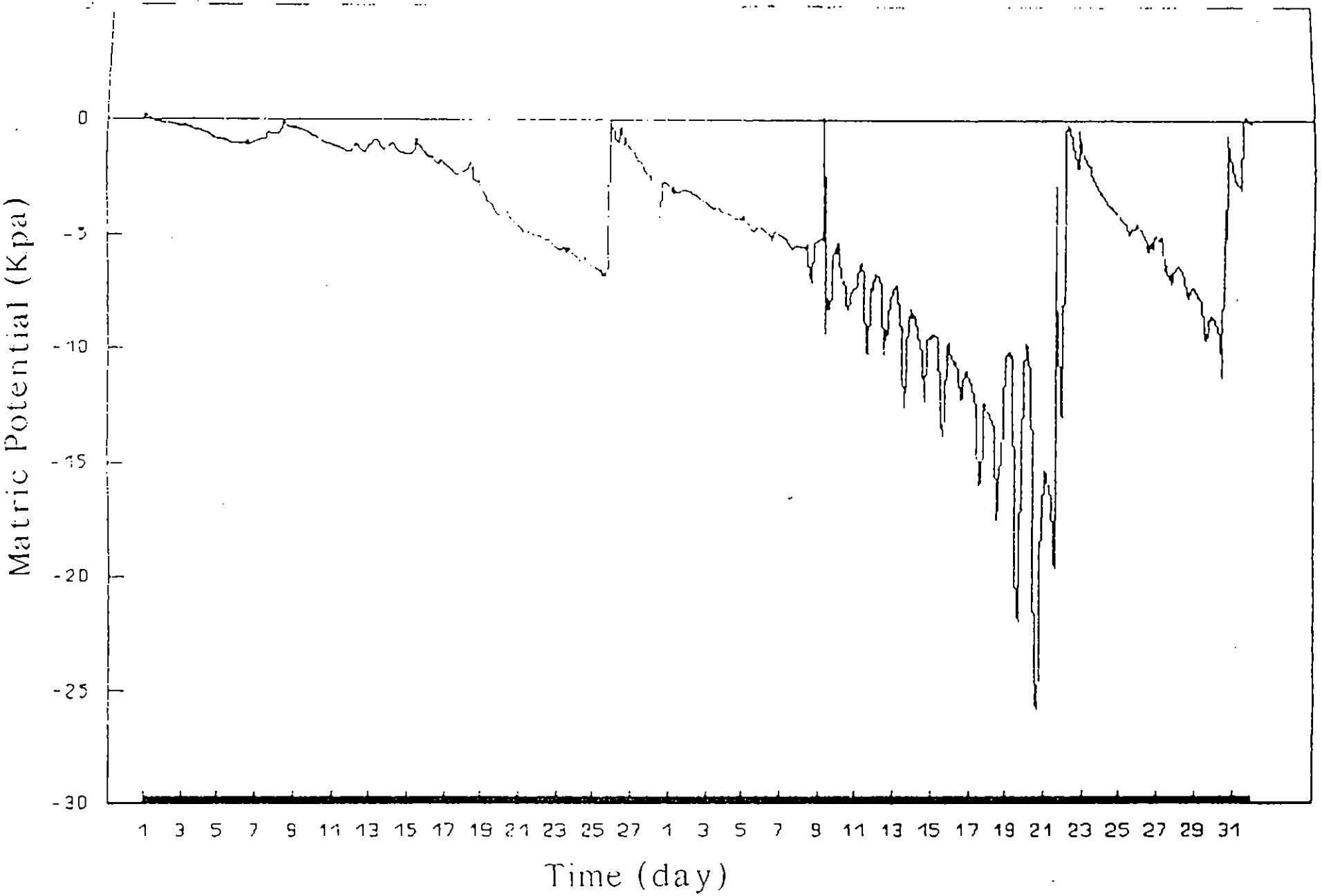


Figure 9. Matric Potentials at 10cm Depth at Wytham From 1st February to 31st March 1993.

a:cumrain

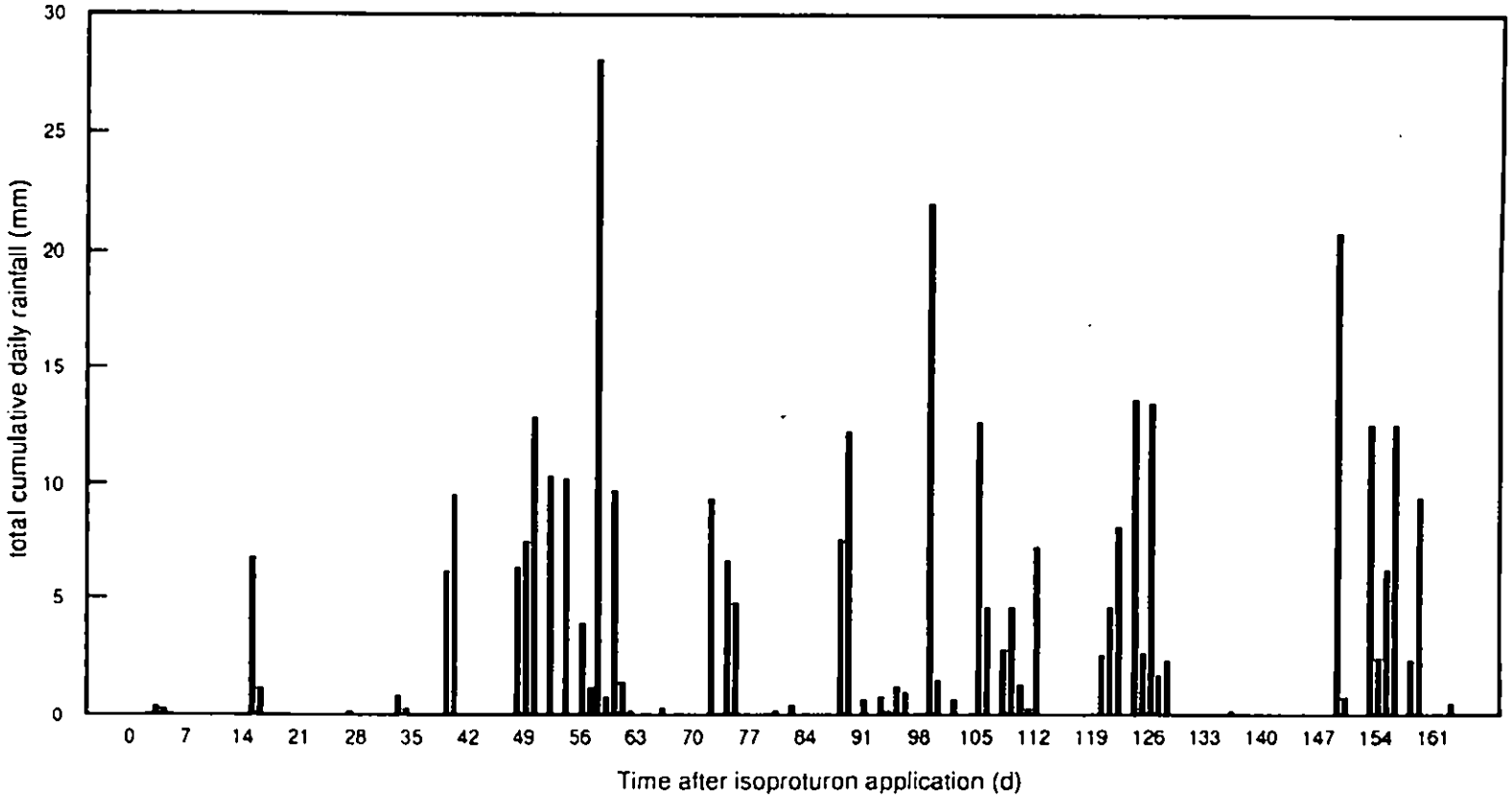


Figure 10. Rainfall data for Wytham beginning 1 April, 1993

a:cumtemp

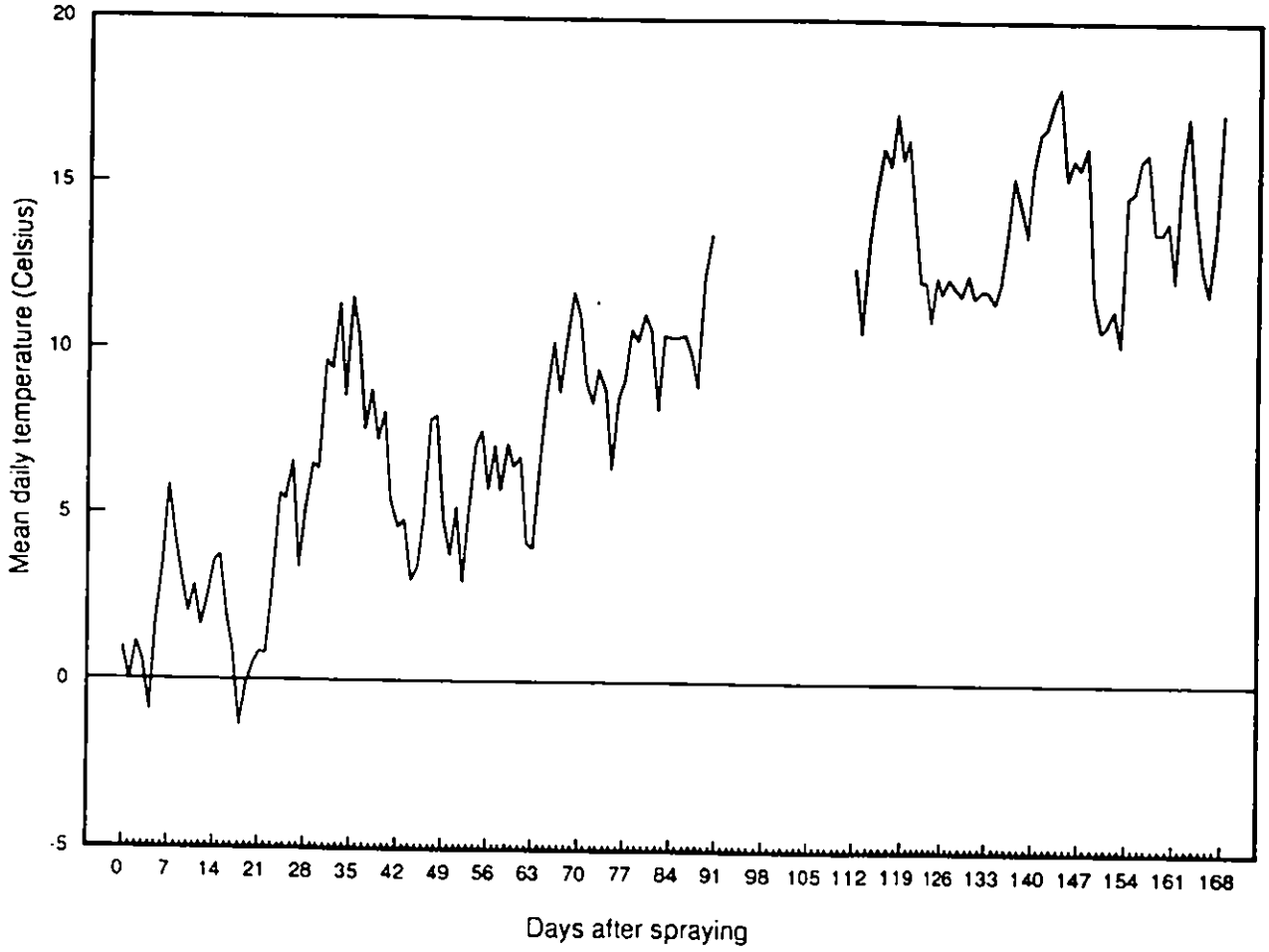


Figure 11. Mean daily temperatures, beginning 10 February, 1993

a:storm1

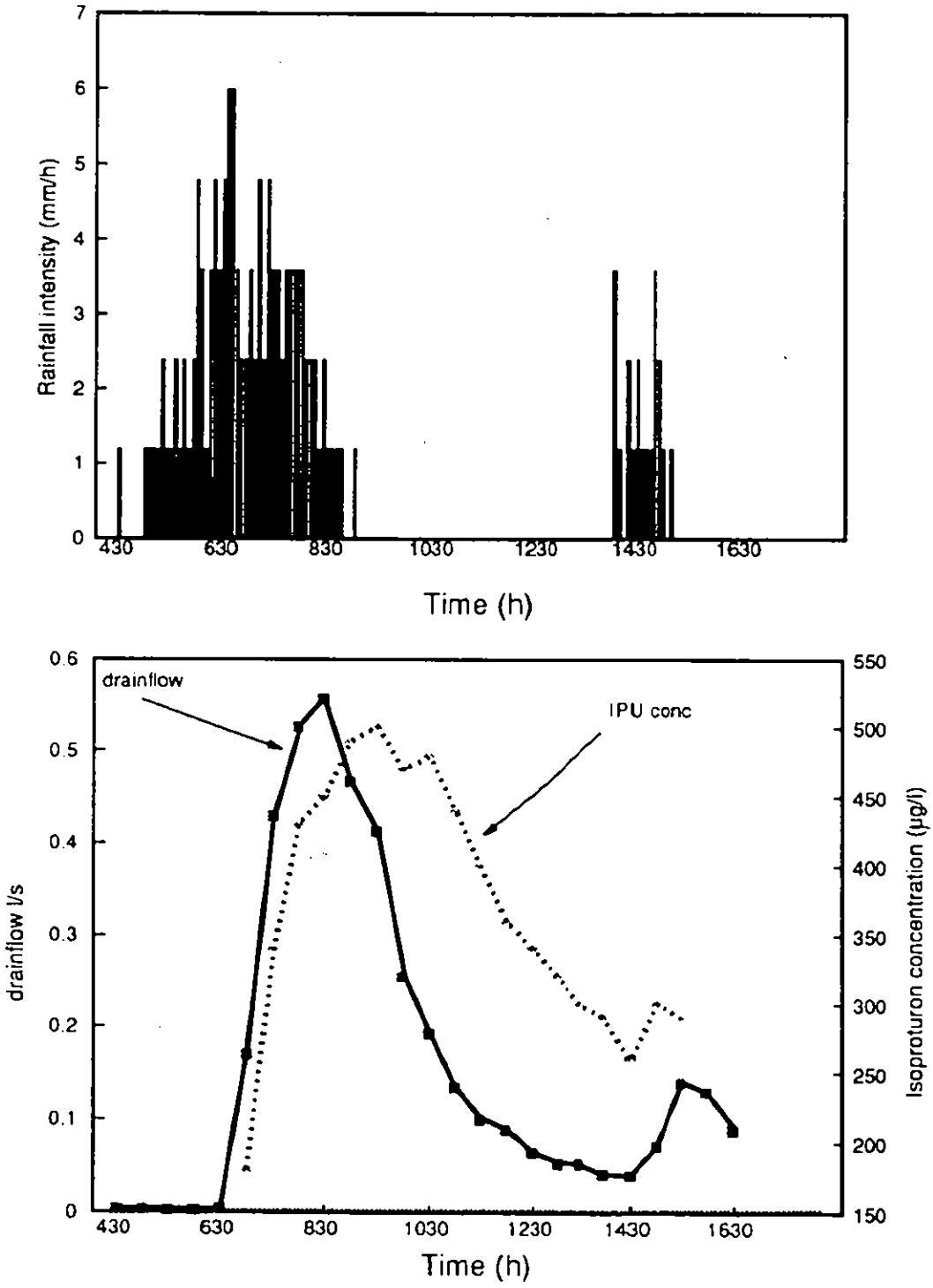
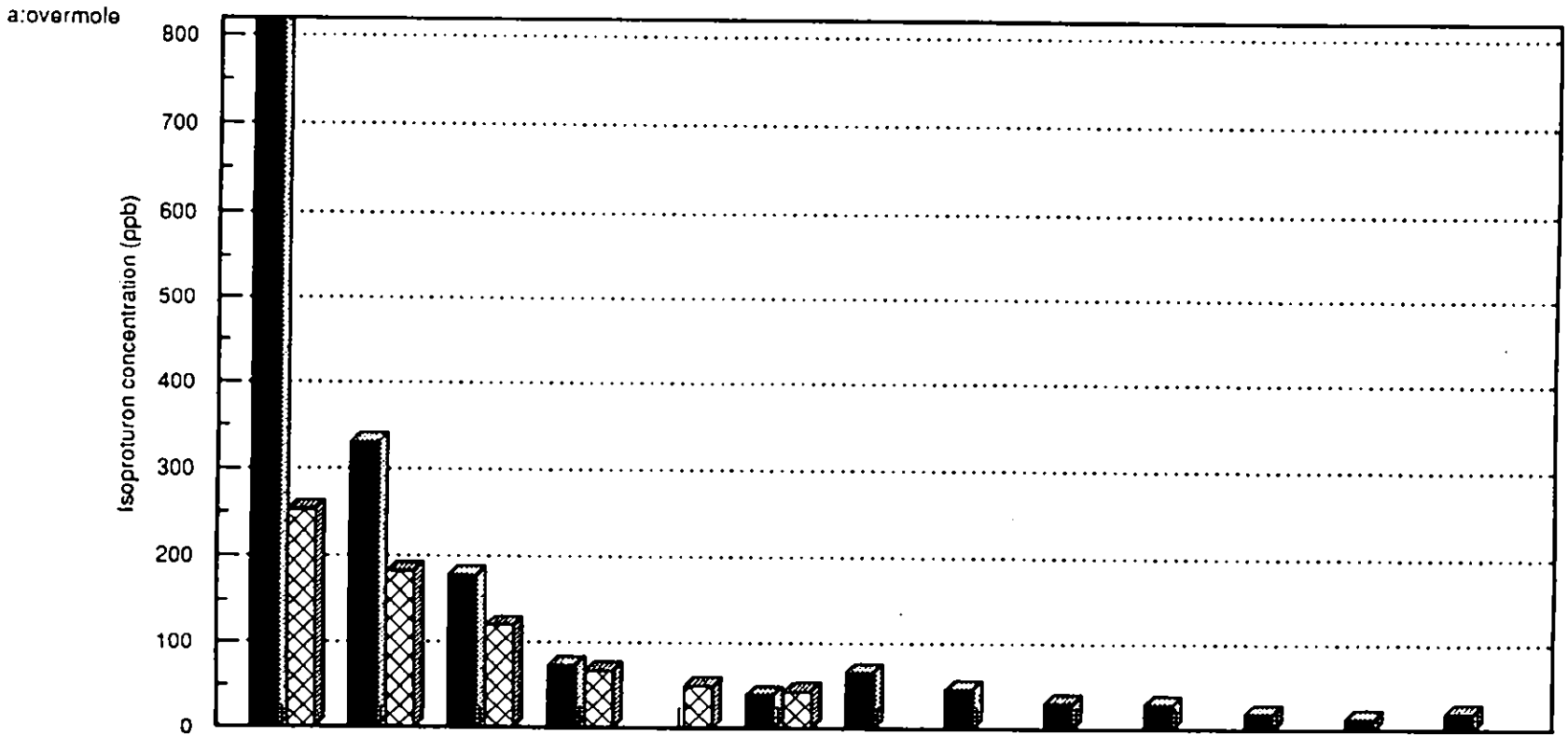


Figure 12. Relationship between rainfall, drain flow and ipu concentration 50 d after ipu application (1,4,93)



Time after isoproturon application (d)	50	56	64	75	78	90	100	106	113	120	124	127	162.
overland flow	817	330	179	73	0	40	66	47	31	30	19	13	20
mole drain	252	183	120	67	50	44	* N/A	N/A	N/A	N/A	N/A	N/A	N/A

Figure 13. A comparison of isoproturon concentrations found in overland flow and mole drainage water
(2 replicates for overland flow and 1-3 for mole drains)

* N/A No water available to collect

A:IPUPTT1

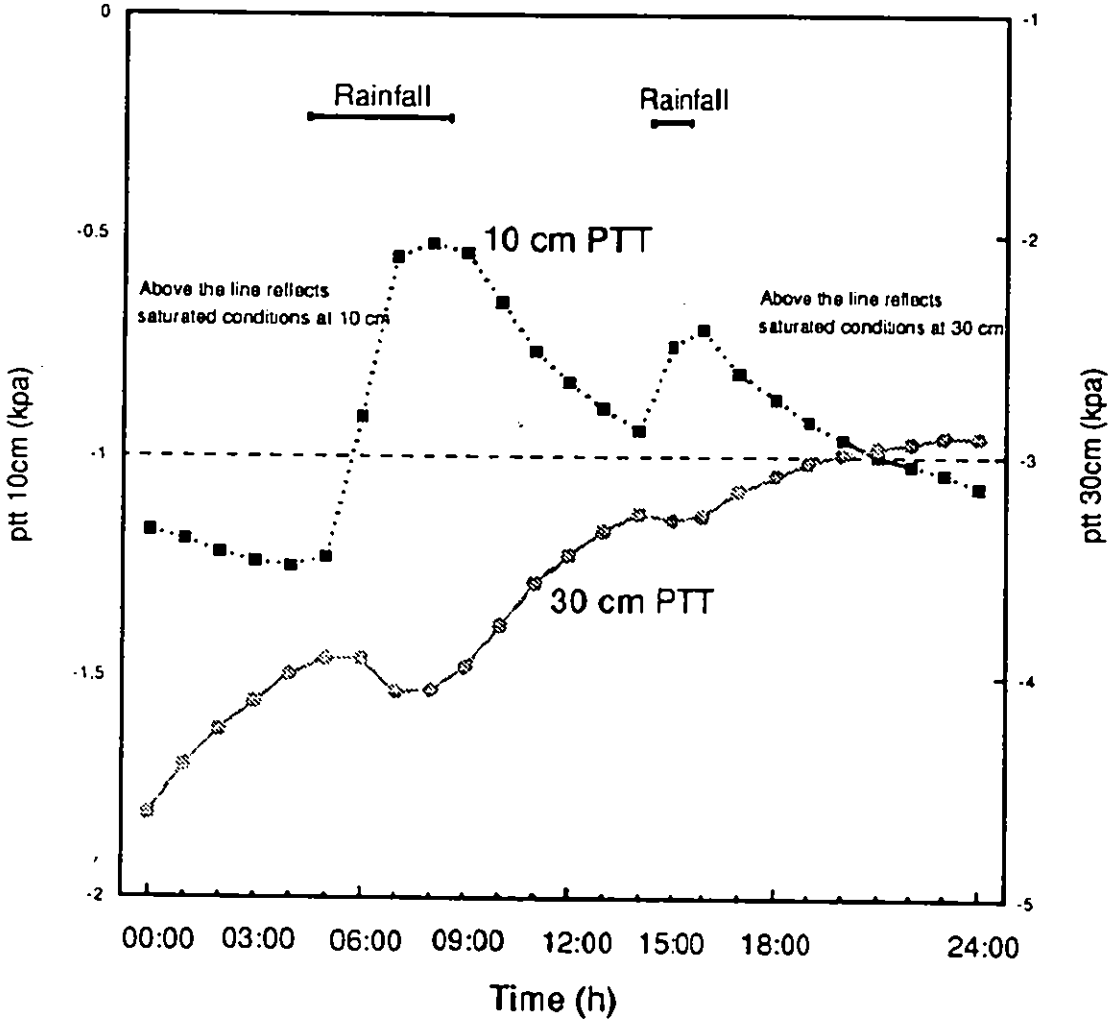


Figure 14. Total Potentials at 10 & 30cm Depths during storm event 50 d after ipu application (1,4,93)

On this occasion the drain flow did not plateau out, suggesting that the maximum capacity for infiltration had not been reached. The field drain demonstrated the typically peaked hydrograph (rapid response to rainfall) which have been noted by (Kneale, 1986; Robinson *et al.*, 1987; Robinson and Beven, 1983) as a characteristic of underdrained clay soils of this type.

Storm event 3 (SE 3) - 3rd April 1993, 52 days after spray day.

Figure 15 describes SE 3 which occurred 2 days after SE 2. Again, as with SE 2, the drainflow associated with that rainfall event has been plotted, along with the concentration of isoproturon present in the drain water.

As with SE 2 there was a delay in the initiation of drain flow after the start of rainfall. It is interesting to note that the rain storm two days previously did wet up the profile and change the antecedent soil moisture condition. PTT data in Figure 16 clearly shows the increase in wetting from unsaturated to saturated conditions at 30 cm. Thus as the drains were flowing under both these conditions, it suggests that drain flow was not influenced directly by soil antecedent moisture status below approximately 10cm from the soil surface.

A further drainflow event occurred (data not shown) which coincided with saturated conditions being measured by the 10 cm PTT on day 54, shown in Figure 16.

Observed conditions after 12 April, 1993 (day 62)

No significant drain flow events were measured from day 62 despite a greater than average amount of rainfall (Fig. 8). The possible reasons for this include the much higher SWD that had to be satisfied, and large cracks, visible through the mole access ports, running lengthways along the base of the mole drains. In addition, the higher radiation at this time of year means a greater potential evaporation rate. The crop being at a mature growth stage would have lead to greater extraction of water from the soil. As shown in Figure 17, which describes the matric potentials at 0.1 m depth during May and June 1993, the rainfall was only enough to bring the point at 10 cm below the surface to saturation for short periods without the creation of a significant "head of water" as observed in previous drainflow events. Although drainflow was not observed during this period some limited overland flow did occur as water was collected from the overland flow traps (Figure 13). Neutron probe data which was collected during this period is shown in Figure 18. A general decrease in water content of the soil can be seen over this period. The occasions on which a transient increase in water content was seen at all depths may be related to rainwater running down the cracks around the neutron probe access tubes.

Leeds-Harrison *et al.* (1986) suggested that the hydraulic conductivity, (K), of cracked soils is much greater than saturated soils, and that the fall in K is very rapid initially as a soil begins to swell under constant saturation. Thus one would expect in saturated conditions the percentage of rainfall bypassing the soil matrix to become drain flow to be far less than in drier conditions. However our data did not show increased amounts of rainwater going to drainflow during the drier period. In the summer other factors as mentioned may prove to dominate in the restriction of drain flow, more so than the swelling of pores associated with wetting.

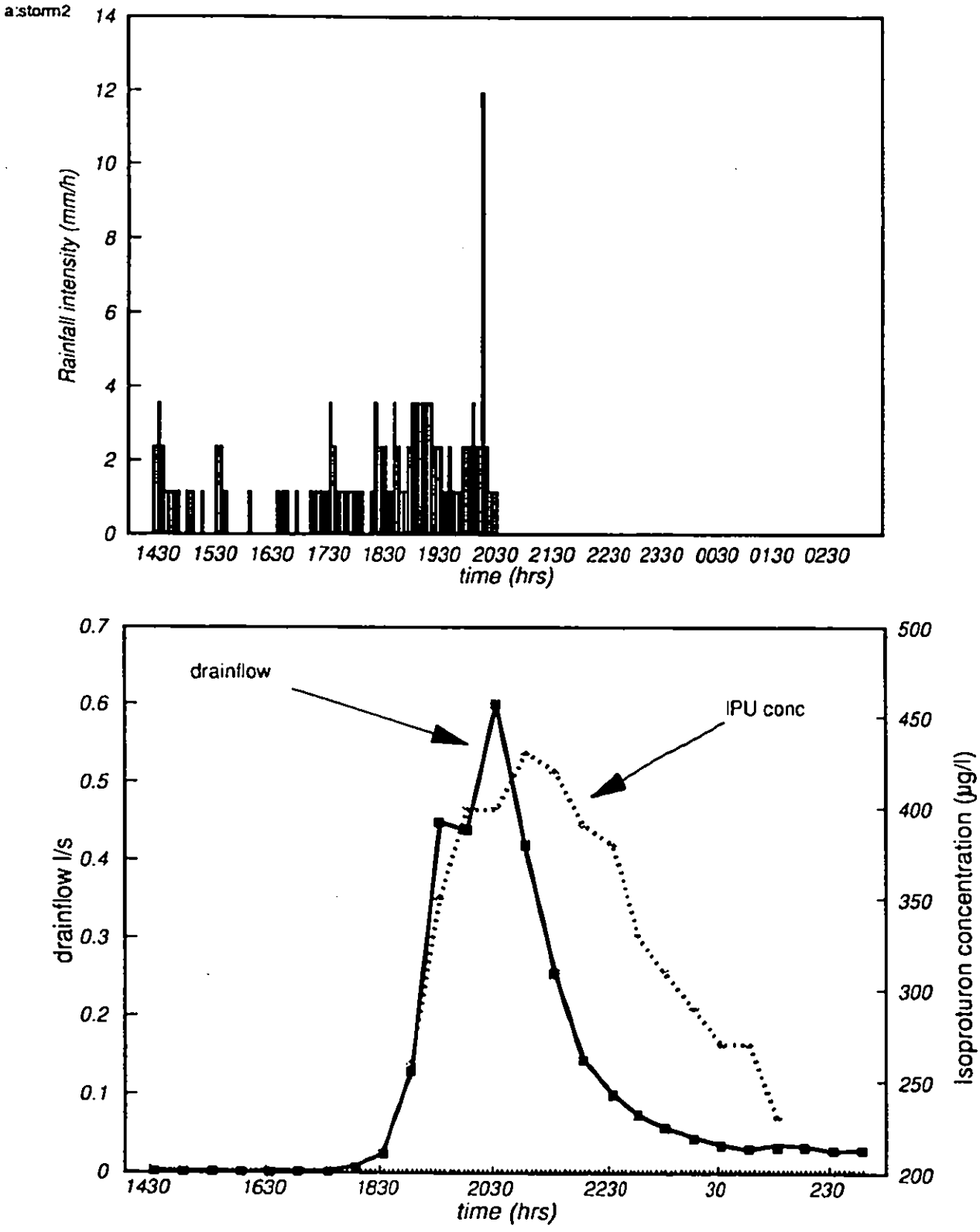


Figure 15. Relationship between rainfall, drain flow and ipu concentration 52 d after ipu application (3,4,93)

a:ipuptt3

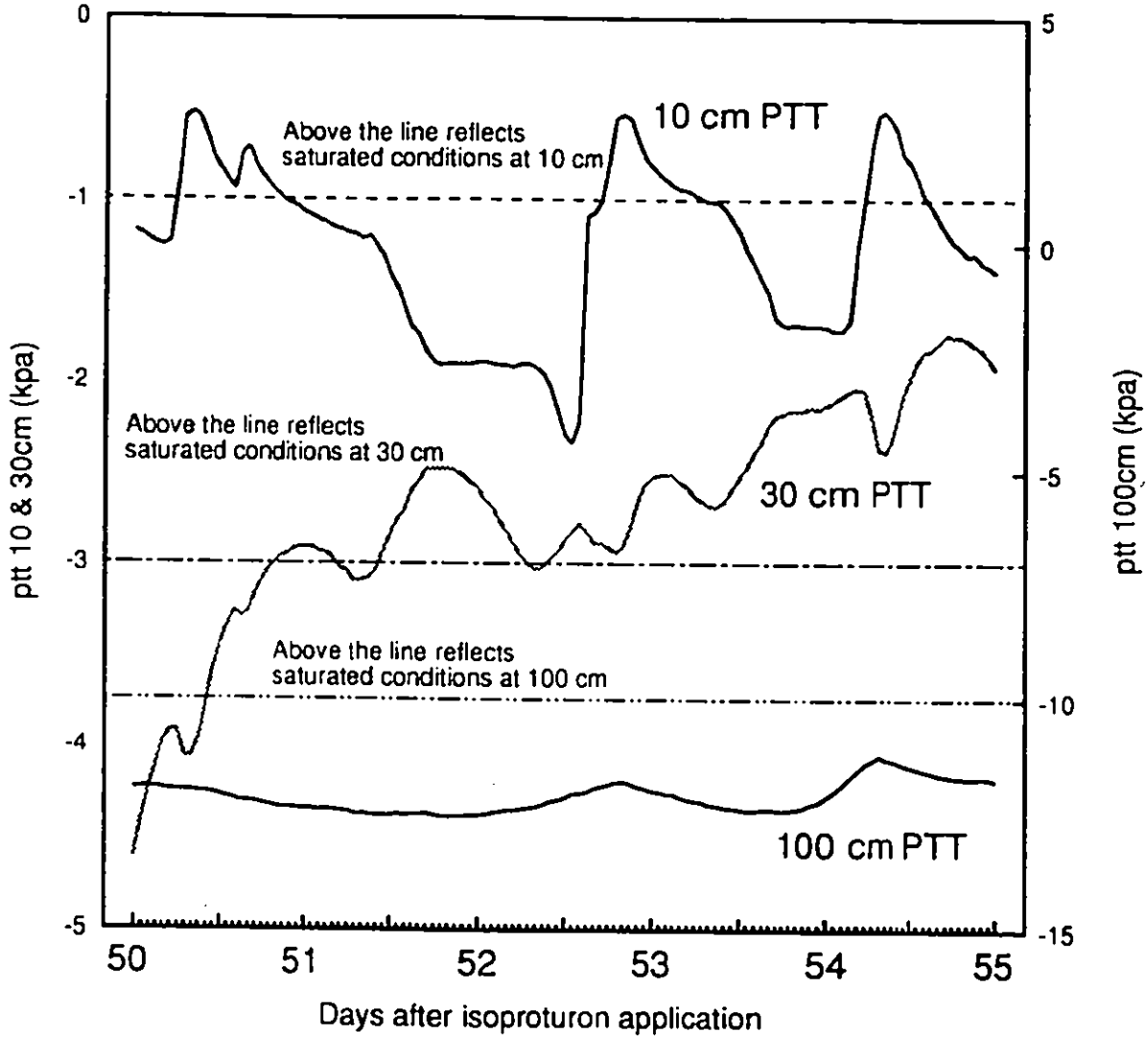


Figure 16. Total potentials at 10, 30 and 100cm depths during rainfall events from April 1st to 5th 1993

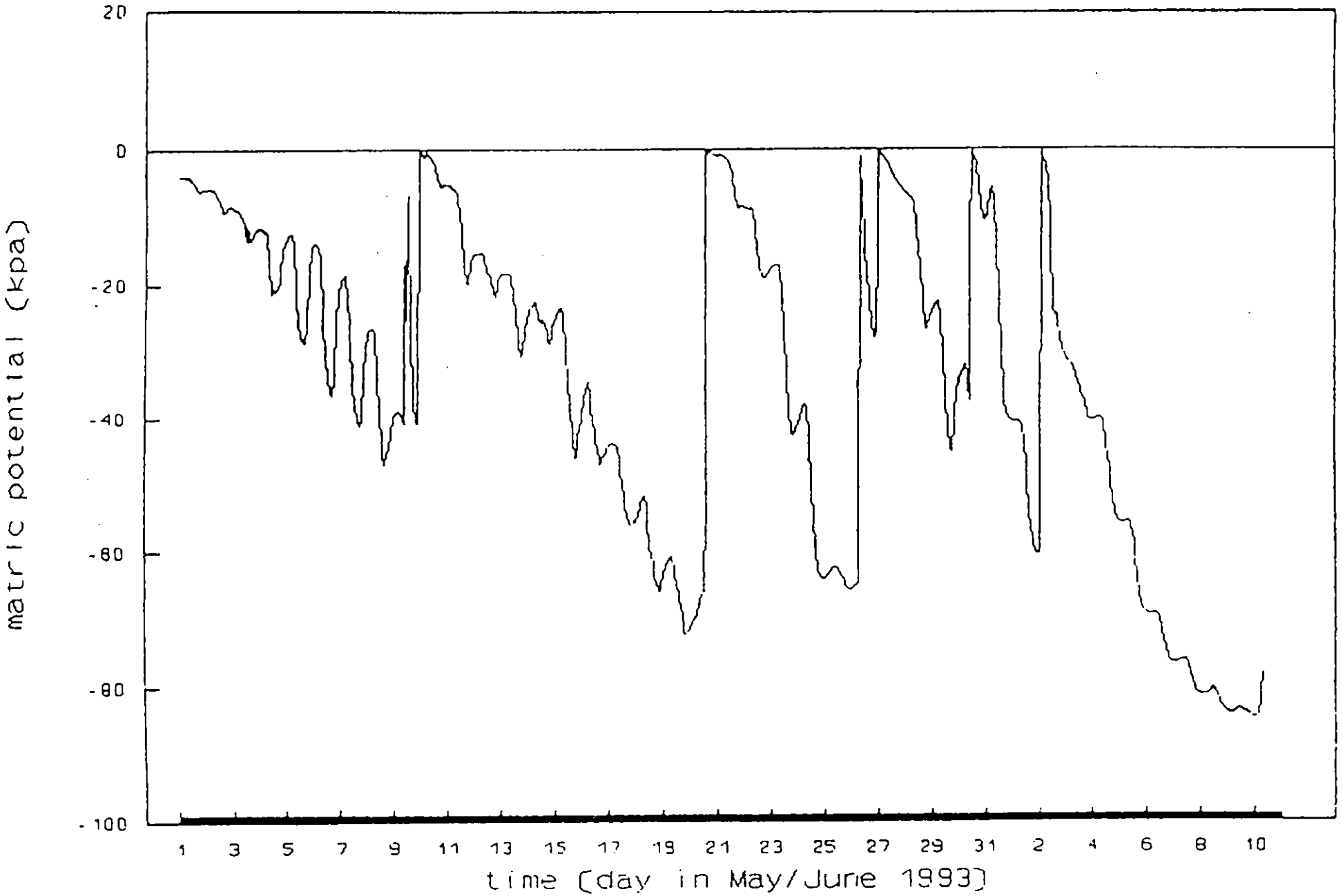


Figure 17. Matric Potentials at 10 cm Depth at Wytham From 1 May to 10 June 1993.

a:NP1

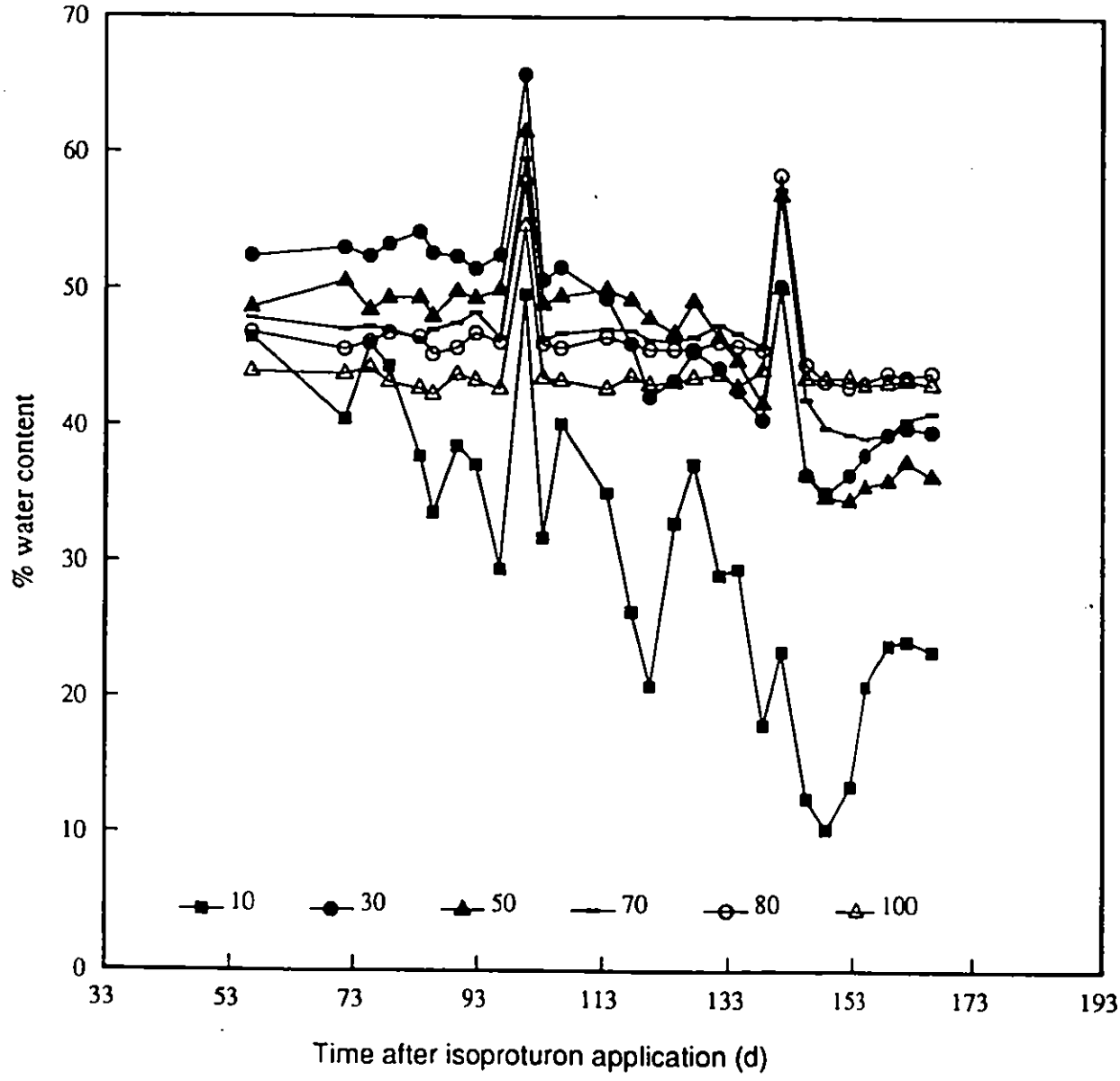


Figure 18. Changes in water content over time as measured by twice weekly neutron probe readings beginning 4 April, 1993.

Table 1 *Comparison of hydrological data from storm events 1, 2 and 3.*

	STORM EVENT 1 6th/7th December 1992	STORM EVENT 2 1st April 1993	STORM EVENT 3 3rd April 1993
Total Storm Rain (mm)	18.3	12.7	10.3
Rainfall exiting as drain flow (%)	17.6	31.9	28.1
Rainfall that satisfies SWD before drain flow can start	-	39% = 4.95 mm	45% = 4.64 mm
% Rainfall accounted for	-	71%	73%

Table 1 gives a comparison between the three storm events, showing the percentages of rainfall that were used to satisfy the SWD, and that which exited as drain flow. This was for a catchment estimated to be 1800 m^2 in size. As can be seen, similar amounts of rainfall (4.5 - 5.0 mm) were needed to satisfy the SWD before drainflow was initiated in April. This is despite the much wetter antecedent conditions below the topsoil for SE 3. The data suggests that soil water antecedent conditions below the surface 10 cm (approx.) are irrelevant to drain function. Approximately 70% of the rainfall for the storm events in April can be attributed to these two processes, leaving 30% still unaccounted for. This 30% may be accounted for by overland flow, sub-surface lateral flow or deep drainage. Process studies in the forthcoming 1993-94 season will attempt to improve our understanding of the in-field soil water balance.

4.2.3 Discussion of factors influencing flow mechanisms

Figures 19 and 20 are attempts to obtain an estimate of the antecedent conditions required to initiate overland flow and drain flow, all flow data being plotted against the equivalent matric potentials at a depth of 0.1 m below the soil surface.

All overland flow events monitored by the overland flow meter occurred only when the matric potential at 0.1 m was greater than zero, ie. when the surface 0.1 m is saturated. The same was true for the drainflow data. Therefore if the surface soil is anything less than saturated, overland flow and drainflow will not occur.

Specifically looking at drainflow it can be seen in Figure 20 that the majority of the points for all drainflow events of > 0.15 l/s (approx.) are located when the soil at 0.1 m depth had on it a positive head of 0.5 kpa. If rainfall is separated into that which did and did not initiate drain flow and plotted against the antecedent soil surface moisture conditions as represented by 0.1 m PTT, Figure 21 can be presented. This figure demonstrates that most rainfall that fell when the soil matric potential at 0.1 m was less than 0.4 kpa did not initiate drain flow; and that rain falling at a surface matric potential greater than 0.4 kpa did initiate drain flow.

However, it can be seen that on some occasions rainfall events caused drainflow when the surface was less than saturated, and some rainfall at surface saturation caused no drainflow. The former can be explained in that the PTT located to monitor surface conditions is at 0.1 m below the soil surface. In reality the conditions for drain flow may require saturation in only

a:pttflow

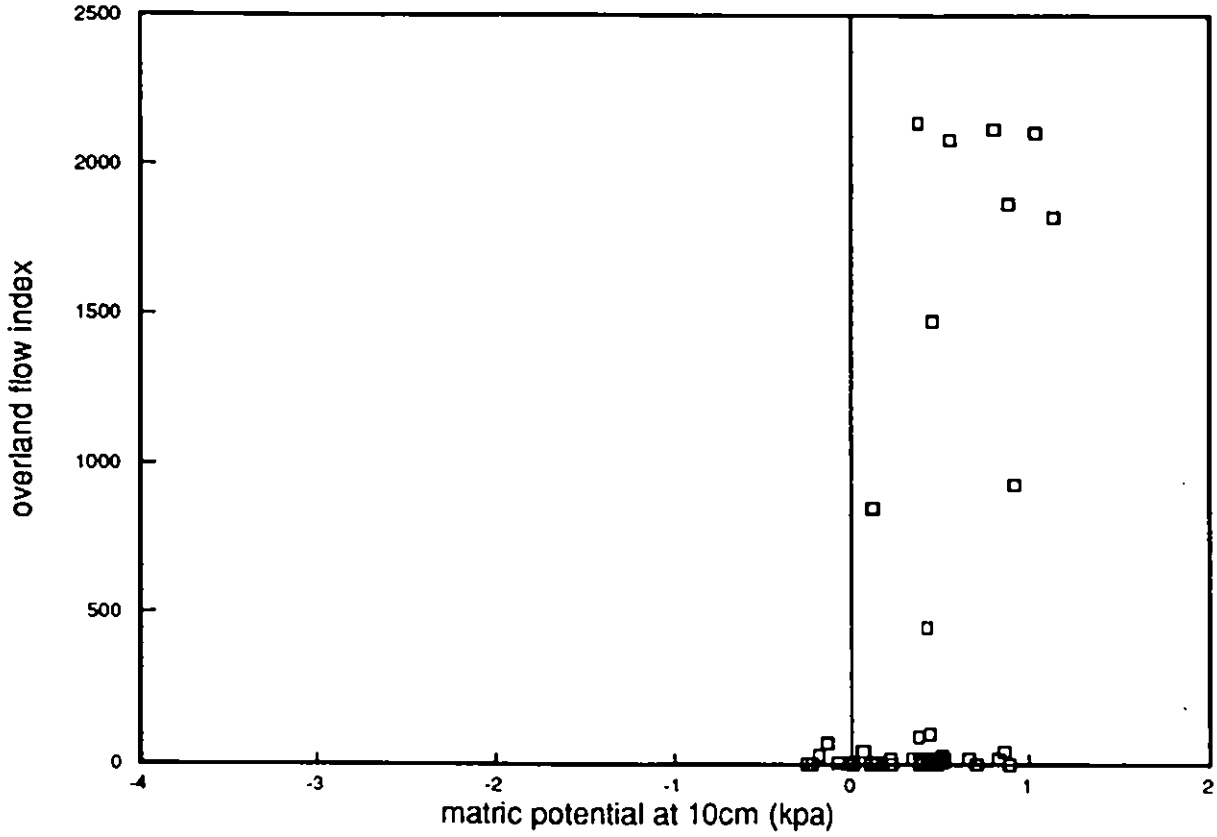


Figure 19. Overland flow events and related soil matric potentials at 10 cm depth

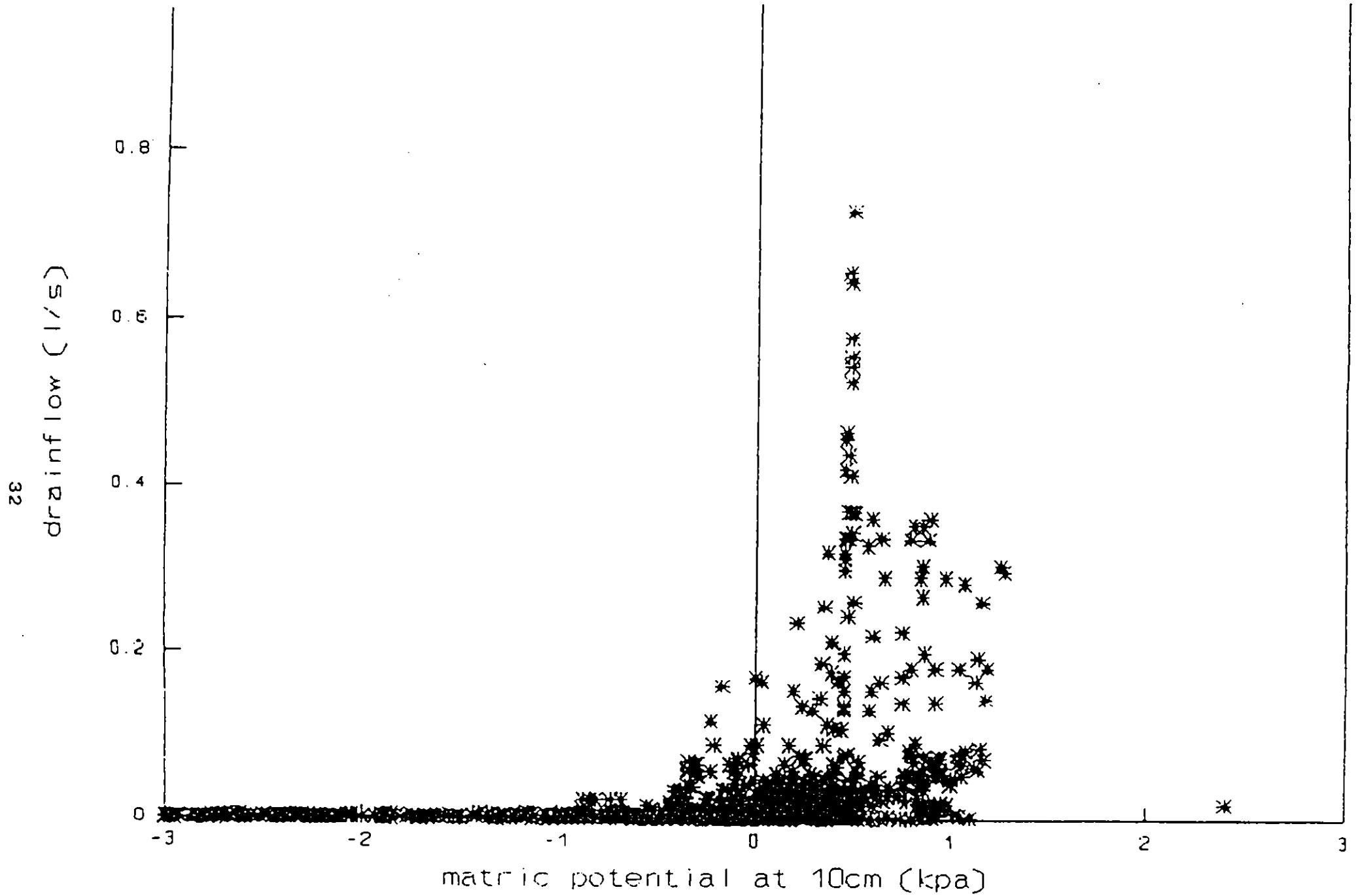


Figure 20. Drain Flow Occurence and Related Soil Matric Potentials at 10 cm Depth.

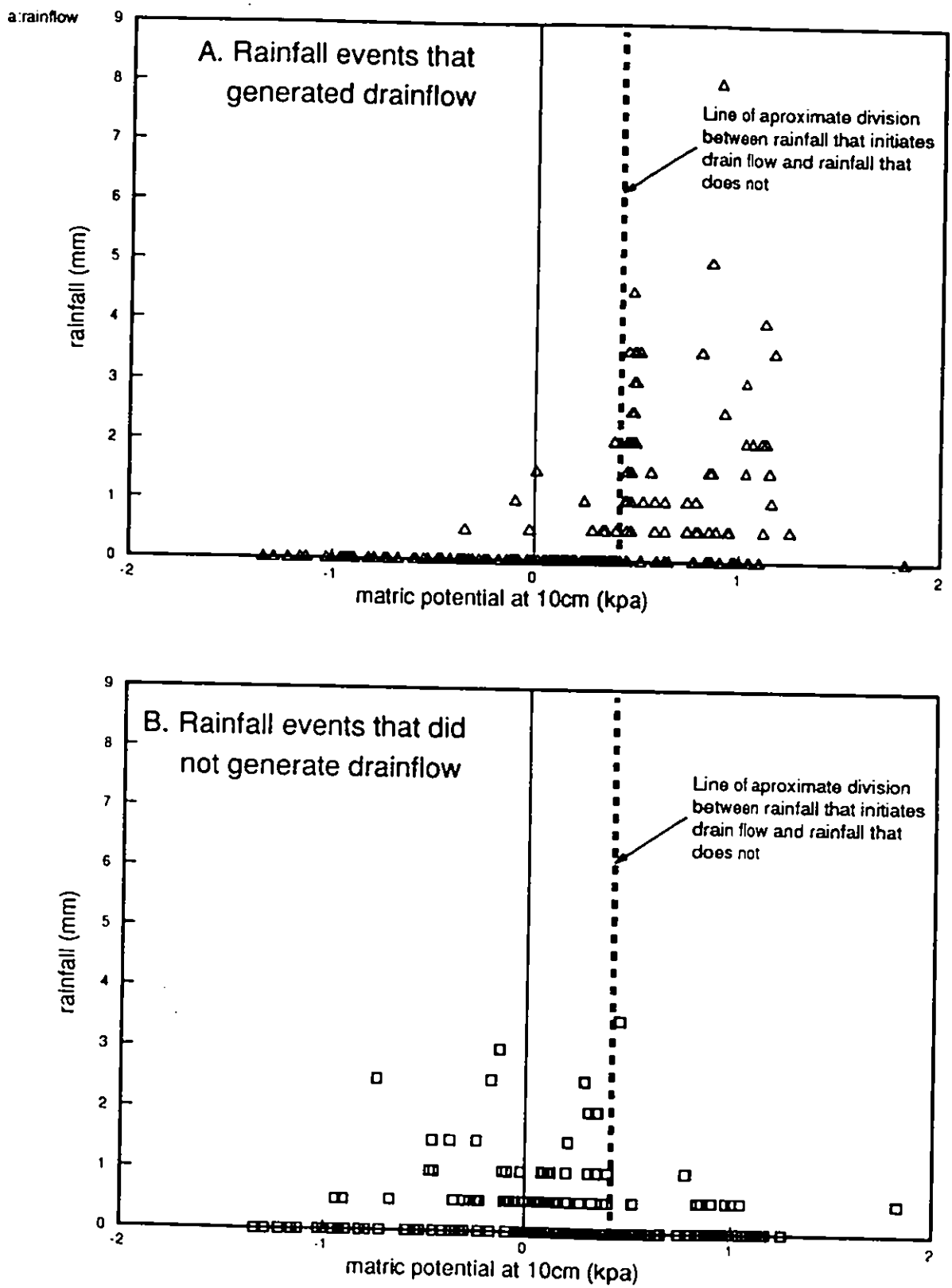


Figure 21. Examination of the relationship between rainfall, antecedant soil moisture conditions at 10 cm and the initiation of drainflow.

the top 0.05 m (for example); surface saturation that would not be monitored by the 0.1 m PTT. The rainfall events at surface saturation that did not cause flow could possibly be secondary rainstorms a few hours after major events when the surface was very wet. A small volume of water would then only initiate trickle flow that would not be recorded.

The distinction between the two groups of rainfall events is shown by the vertical dashed line in Figure 21 and suggests the initiation of a saturated layer before major water fluxes to the mole drains can begin. The presence of this saturated layer is likely to form the locus for lateral interflow, even under largely unsaturated conditions at depth, which may divert excess water laterally towards the moling fissures. This induction of lateral flow in the topsoil, by the rise in potential, towards the fissures over the mole drains has been noted by Leeds-Harrison *et al.* (1982).

Evidence that water in the saturated topsoil moves laterally was provided by use of bromide as a tracer at Wytham. 1 l of 10,000 ppm bromide placed 1.5 m upslope of the 25 cm suction samplers can be detected 56 days after application following the major rainfall events beginning on day 50 (see Figure 22). In addition the same amount of tracer placed over mole drain 25 could also be detected in the sump placed in the mole drain during the main rain events 49-50 days after application. A small proportion of the tracer appeared to have moved laterally to the next mole drain 3 m downslope from where the tracer was applied (see Table 2).

Table 2 *Vertical movement of tracer into mole drains*

Time after application (d)	50	56	64
mole 25	13,600	6,000	3,100
mole 24	1,000	400	50
mole 22	50	100	50

Concentrations given in ppb

10,000 ppm Bromide tracer applied directly above mole 25. The mole drains are 50 cm below the surface. Mole drains 24 and 22 were 3 and 9 m respectively downslope

Figure 23, which is based on results from this first field season, gives a schematic overview of the principal routes of water flow over, within and below the soil at Wytham; and thus shows the possible routes of pesticide transit to the catchment surface and sub-surface drainage systems.

4.3 PESTICIDE PERSISTENCE AND TRANSPORT

4.3.1 Variation in pesticide degradation with depth

Detailed pesticide sorption studies have not yet commenced with Wytham material. A preliminary experiment on isoproturon degradation (Figure 24) has been carried out using ^{14}C labelled isoproturon with topsoil (upper 3 cm) and soil from the 'B' horizon (40 cm).

a:su25br

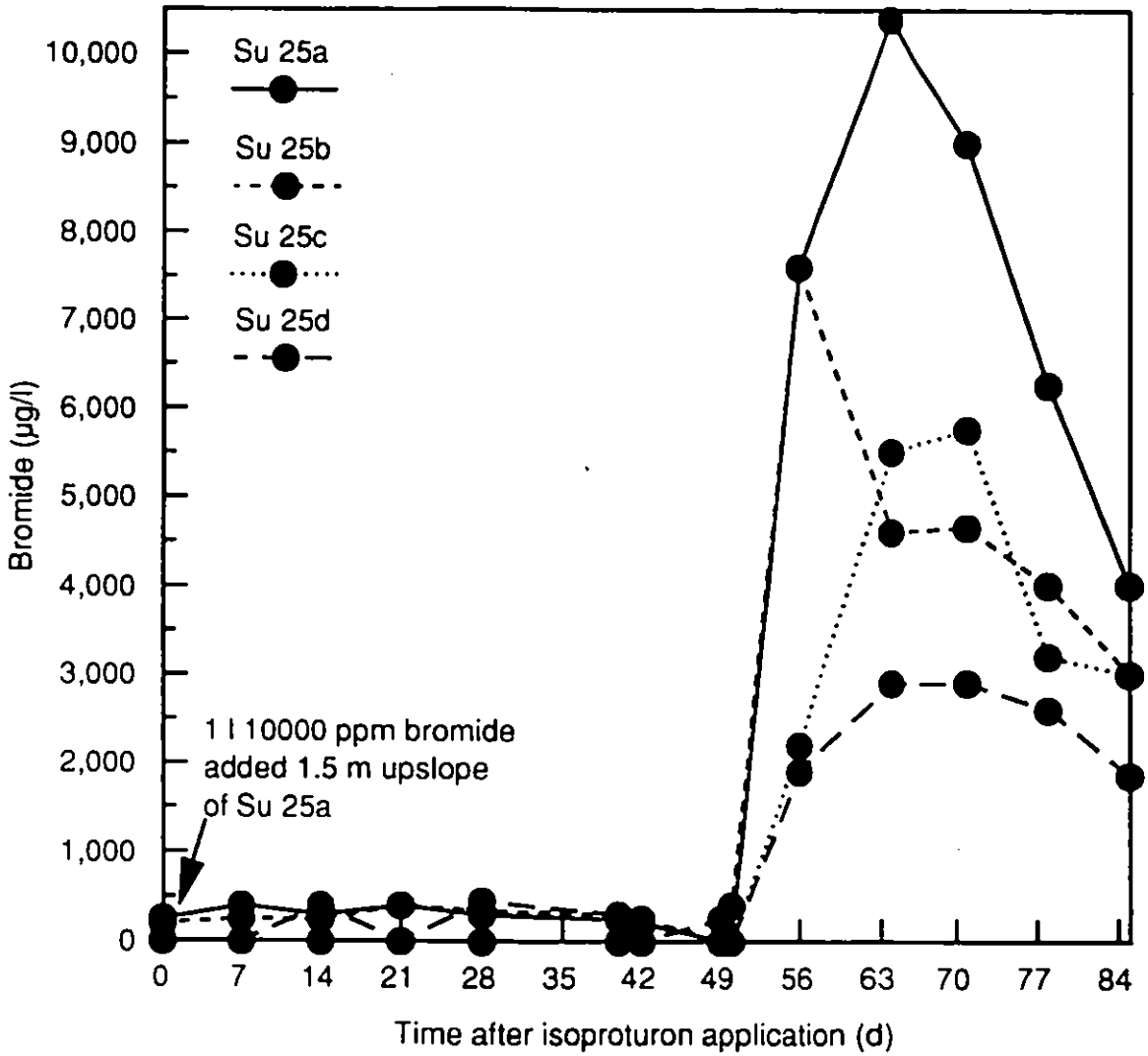


Figure 22. Lateral tracer movement towards 25 cm suction samplers

a:wyflow3

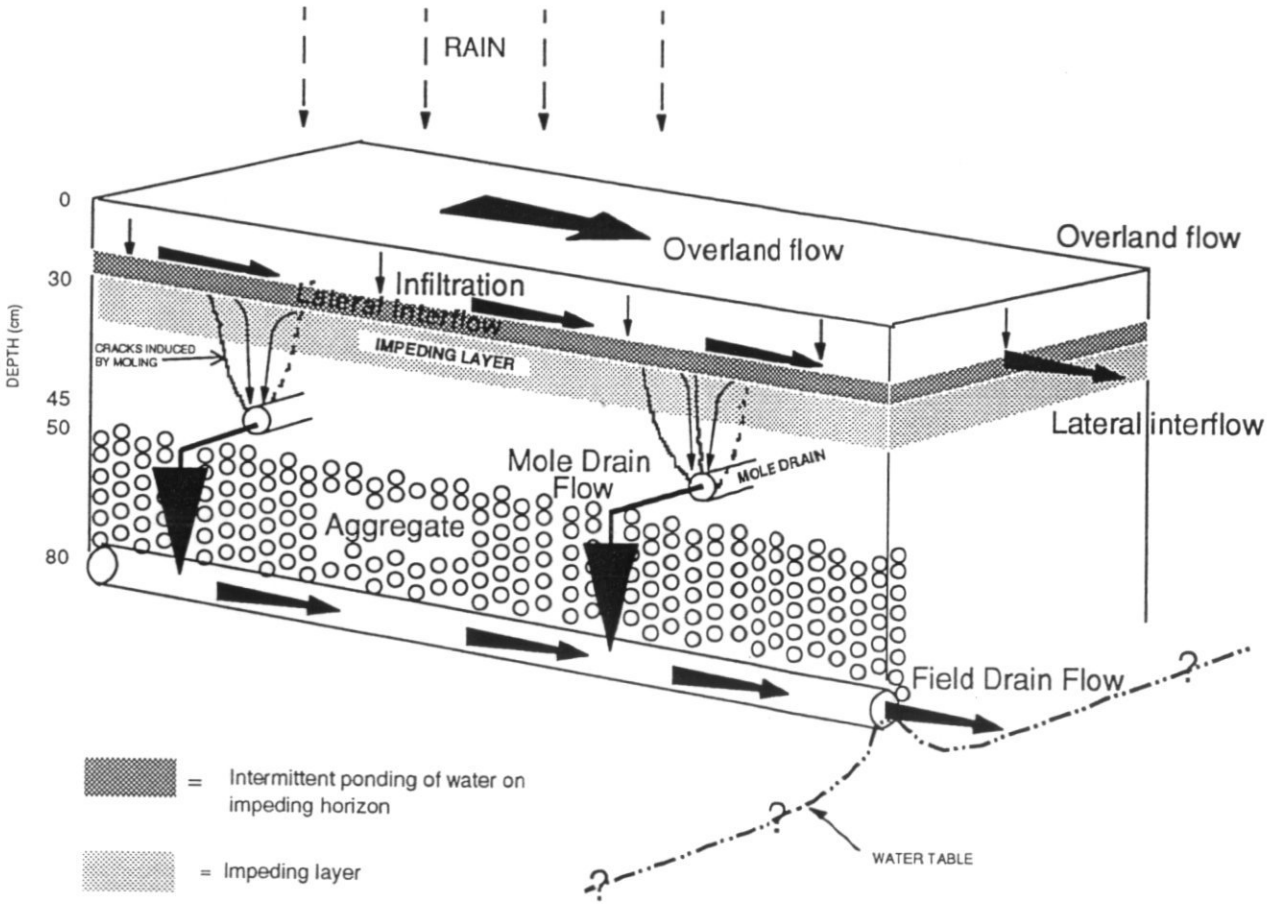


Figure 23. Schematic diagram of principal flow routes of water through and over the soil at Wytham

a:wydeg2a

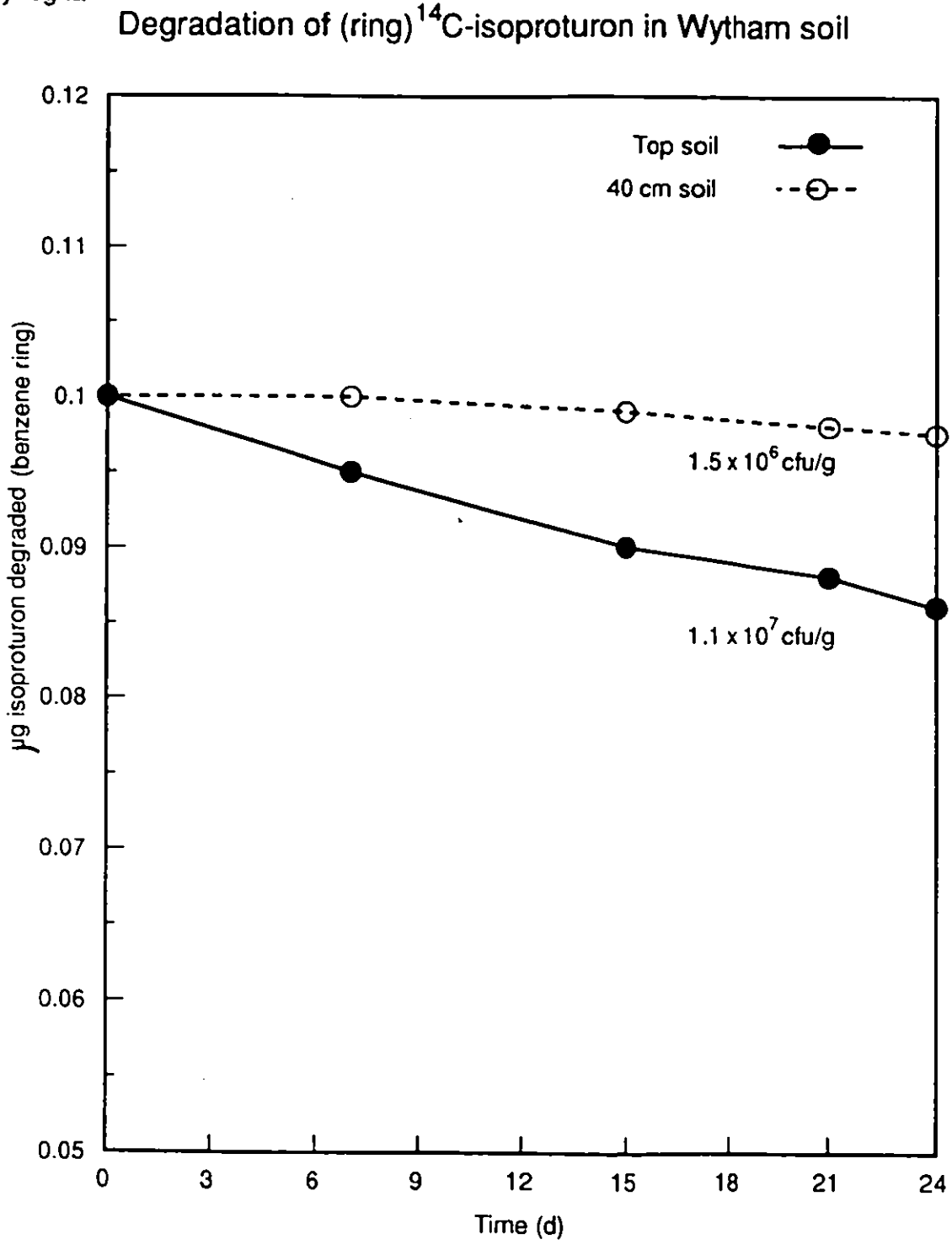


Figure 24. Degradation of ^{14}C-isoproturon (0.01 mg/kg) at 20 °C . Soil was air-dried before re-wetting to original moisture content (31.5 % for top soil and 21.6 % for 40 cm soil) with a solution of 10 mM Ca Cl_2 containing ^{14}C-isoproturon
(6 observations per mean)

Degradation is signalled by the complete metabolisation of the benzene ring and the release of $^{14}CO_2$, so the degradation rates cannot be compared to true half-lives. However, the potential to degrade the compound in the lower horizon is much reduced in comparison to the topsoil, only 2 of the 6 replicates showing any degradation. This also suggests that the degradation potential at depth is likely to be much more variable in a lateral sense when compared to the topsoil. It may be appropriate to study the anaerobic degradation also at this depth.

Analysis of the number of viable aerobic heterotrophs at depth shows a tenfold reduction with depth from 1.1×10^7 to 1.5×10^6 cfu/g. The higher clay content at depth (Jarvis and Hazelden, 1982) particularly of smectite (Figure 6) may also influence degradation through adsorption of the pesticide, making it less available to bacteria as noted by Sims *et al.*, (1992).

4.3.2 Mini-lysimeter data on pesticide transport

Intact soil cores were taken from Wytham but considerable problems were encountered due to the shrink-swell nature of the clay soil and the propensity of the rain/irrigation water to move down the edge of the column. The methods being used are now being improved by the use of vaseline to reduce preferential flow of water and solutes down gaps between the soil core and the PVC or aluminium containers in which the soil is held.

4.3.3 Persistence of residues in the field

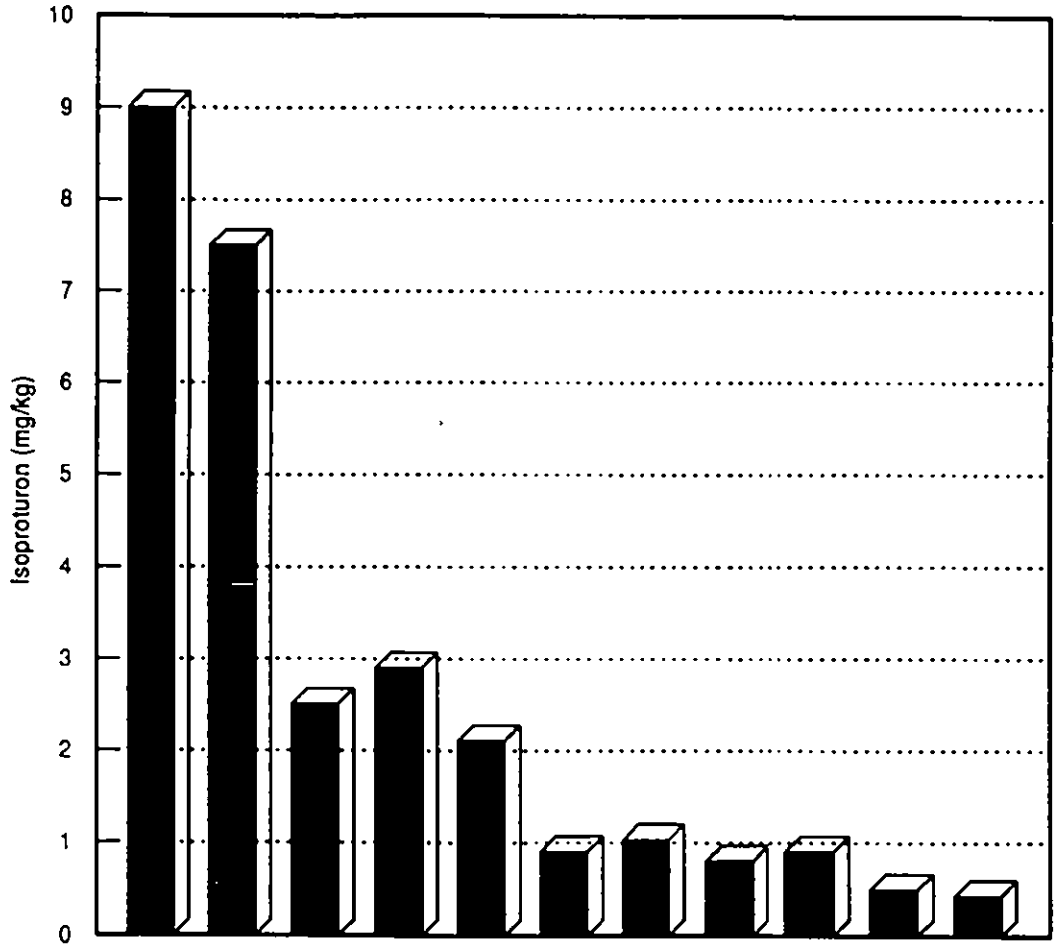
Table 3 shows the even distribution of pesticide over a 12 m long sampling area on the spraying day, which indicated a remarkably even application. The measurement of soil residues showed a good agreement between the replicates within each square metre that was sampled. The decline in amount over time (Figure 25, see also Table 10) gives a curve which suggests a DT_{50} in the region of 30 days, as expected. However, when the pesticide concentration was reduced to the 1 mg/kg level in soil it persisted for a longer period than would have been predicted by the DT_{50} assumption of 30 d. This phenomena of increased persistence of a small proportion of the soil residues was also observed with isoproturon by Mudd *et al.* (1983) in a sandy loam soil. This may be because this residual pesticide is protected in some way from degradation and is not bio-available. An alternative explanation is that degradation was reduced due to increasing moisture stress in the drier summer months.

Table 3 *Distribution of isoproturon (expressed as kg/ha) at Wytham on spray day, 10th February 1993, measured by a series of filter paper discs spread across the plot (30 m).*

	A	B	C	D	E
1	2.67	2.25	2.95	2.62	2.17
2	2.43	2.61	3.06	2.53	1.92
3	2.71	2.37	2.76	2.26	1.91
4	2.59	2.12	2.79	2.38	1.97

Overall mean = 2.45 kg/ha
SD = 0.33

a:residue2



Time after application (d)	7	21	35	49	64	78	100	113	127	141	155
Isoproturon concentration (mg/kg)	9.00	7.50	2.50	2.90	2.10	0.90	1.03	0.80	0.90	0.49	0.43

Figure 25. Isoproturon present in the top 2 cm of soil at Wytham

4.3.4 Isoproturon in overland flow water

Whilst data were collected on isoproturon concentrations in overland flow water, the total loss of pesticide from the field plot by this route cannot be estimated, as the overland flow traps collected water from an unknown and variable area. The data does, however, give an indication of the amounts of pesticide that could be mobilised and transported from the soil surface. This is potentially the same water that could enter a macropore and find its way to the drainage system. Between day 50 and 90, rainfall events generated both overland flow and drainflow, but from 90 d, rainfall generated overland flow without drainflow (see Figure 13). The chloride and sulphate concentrations found in the overland flow water were lower than that in the soil water (up to 50% less for chloride) collected by the suction samplers (see Tables 4, 5 and 6). Clearly the overland flow that occurred during this period of May to July would have been limited in its extent by the large shrinkage cracks that were developing during this period. The small volumes of 500-100 ml collected by the 2 m traps during this period would probably have been from rainwater that collected immediately in front of the traps. It is interesting to speculate on the fate of the isoproturon carried in overland flow water and deposited within shrinkage cracks. The potential for isoproturon degradation in the lower horizon would appear to be very low, as indicated by the ^{14}C-isoproturon degradation experiment (see Fig. 24). Possibly this isoproturon is trapped within the matrix for many years, it may possibly reach the groundwater or leak into the drains in succeeding seasons.

Table 4 *Isoproturon and anions in the overland flow traps*

Days from isoproturon application	50	56	64	75	90	100	106	113	120	124	127
OFT1 isoproturon	1,100	330.0	200	95.0	61.0	102.0	62.0	NA	30.0	NA	NA
OFT1 chloride	11	6.5	3	3.5	4.0	5.0	4.0	NA	10.5	NA	NA
OFT1 sulphate	26	16.5	8	6.5	8.0	13.5	11.0	NA	11.0	NA	NA
OFT1 nitrate	>50	>50.0	>25	>25.0	4.6	>25.0	>25.0	NA	21.0	NA	NA
OFT2 isoproturon	535	330.0	158	52.0	20.0	30.0	33.0	31	NA	18.8	13.0
OFT2 chloride	10	6.0	3	4.5	2.5	3.5	2.5	50	NA	7.0	5.5
OFT2 sulphate	23	14.5	2	7.0	6.0	7.5	9.0	7	NA	8.5	7.0
OFT2 nitrate	>50	>25.0	>25	>25.0	0.6	>25.0	8.6	>25	NA	5.2	5.2

Key
NA No determination possible
>25.0 Above highest standard

Concentrations given as µg/l for isoproturon and mg/l for anions

Table 5 *Anions in 25 cm suction samplers*

Days from ipu application	28	40	42	49	50	56	64	71	78	85	100	113
(a) bromide	0.30	0.25	0.20	NA	NA	7.6	10.4	9.00	6.25	4.00	2.70	0.8
(a) chloride	37.00	30.00	31.00	NA	NA	23.0	16.5	16.50	15.00	18.50	16.00	4.0
(a) sulphate	46.00	42.00	44.00	NA	NA	31.0	31.0	31.00	26.00	26.00	22.00	19.0
(a) nitrate	19.00	>25.00	>25.00	NA	NA	>200.0	176.0	120.00	63.00	20.00	>50.00	6.2
(b) bromide	0.36	0.30	0.25	NA	0.4	NA	4.6	4.60	4.00	3.00	2.05	NA
(b) chloride	28.00	30.00	28.00	NA	33.0	NA	25.0	23.00	19.00	18.00	19.00	NA
(b) sulphate	19.00	27.00	28.00	NA	30.0	NA	28.0	27.00	22.00	18.50	17.50	NA
(b) nitrate	3.40	>25.00	>25.00	NA	>50.0	NA	>100.0	>75.00	50.00	17.00	>25.00	NA
(c) bromide	NA	NA	NA	0.25	NA	2.7	5.5	5.75	3.20	3.00	NA	NA
(c) chloride	NA	NA	NA	27.00	NA	26.0	21.0	22.00	13.00	15.00	NA	NA
(c) sulphate	NA	NA	NA	34.00	NA	31.0	27.0	25.00	18.00	19.00	NA	NA
(c) nitrate	NA	NA	NA	>25.00	NA	>50.0	>125.0	>125.00	42.00	26.00	NA	NA
(d) bromide	0.45	0.30	NA	NA	NA	1.9	2.9	2.90	2.60	1.85	0.75	NA
(d) chloride	30.00	29.00	NA	NA	NA	20.0	18.5	18.50	16.50	17.50	10.00	NA
(d) sulphate	23.00	29.00	NA	NA	NA	26.0	24.0	25.00	15.50	15.50	17.50	NA
(d) nitrate	1.80	>25.00	NA	NA	NA	>25.0	>50.0	44.00	1.60	0.50	>25.00	NA

Key
NA No water collected
>25.00 Above highest standard

Concentrations given as µg/l

4.3.5 Isoproturon in the soil water collected by the suction samplers

Data from the suction samplers showed the presence of large amounts of pesticide at depth after the rain event 16 days after application (see Table 7). The suction sampler data must be viewed with great caution as bromide tracer added on day 35 in the immediate vicinity around the 50 and 75 cm suction samplers was detected after only 5 days by all of these samplers. This suggested that water could enter their silica flour 'pots' by running down along the length of the suction sampler directly from the soil surface. In other words, the suction samplers themselves acted as macropores. However, the suction samplers must have interacted to some degree with the surrounding soil pore water as the anion concentrations detected by these instruments were greater than those found in overland flow (see Tables 5 and 6).

Table 6 *Anions (mg/l) in 50 and 75 cm suction samplers*

	28	35	40	42	49	50	56	64	71	78	85	100
50 (a) bromide	NA	0.20	24.0	22.00	NA	12.4	5.00	NA	NA	NA	NA	NA
50 (a) chloride	NA	32.00	26.0	27.00	NA	31.0	17.50	NA	NA	NA	NA	NA
50 (a) sulphate	NA	33.00	28.0	27.00	NA	30.0	29.00	NA	NA	NA	NA	NA
50 (a) nitrate	NA	>25.00	30.0	32.00	NA	88.0	>100.00	NA	NA	NA	NA	NA
50 (b) bromide	0.15	NA	NA	4.50	NA	2.9	NA	2.05	NA	1.50	NA	1.05
50 (b) chloride	35.00	NA	NA	38.00	NA	36.0	NA	40.00	NA	32.00	NA	33.00
50 (b) sulphate	36.00	NA	NA	42.00	NA	37.0	NA	50.00	NA	48.00	NA	41.00
50 (b) nitrate	18.40	NA	NA	23.00	NA	>50.0	NA	>25.00	NA	>25.00	NA	>25.00
75 (a) bromide	0.10	0.10	1.2	1.05	0.65	NA	2.05	0.95	2.9	1.60	0.80	0.65
75 (a) chloride	26.00	27.00	32.0	32.00	34.00	NA	21.00	11.00	18.5	24.00	21.00	24.00
75 (a) sulphate	38.00	38.00	42.0	39.00	50.00	NA	39.00	29.00	25.0	48.00	26.00	29.00
75 (a) nitrate	>25.00	>25.00	>25.0	>25.00	>25.00	NA	>25.00	>25.00	44.0	>25.00	64.0	25.00
75 (b) bromide	0.10	0.15	31.0	25.00	NA	8.8	NA	1.40	0.9	0.85	1.45	1.10
75 (b) chloride	41.00	50.00	50.0	47.00	NA	31.0	NA	13.00	16.0	17.50	28.00	37.00
75 (b) sulphate	>50.00	50.00	100.0	90.00	NA	65.0	NA	27.00	32.0	25.00	56.0	50.00
75 (b) nitrate	>25.00	>25.00	45.0	72.00	NA	110.0	NA	>25.00	>25.0	>25.00	42.0	25.00

Key
NA No water collected
>25.00 Greater than highest standard

Concentrations given as µg/l

Table 7 *Isoproturon in the suction samplers*

Days from Ipu application	7	14	21	28	35	40	42	49	50	56	64	71	78	85	100	113
Su 25a	19.8	9.3	73.0	350.0	NA	340.0	200.0	80	NA	170	129	151	163	112	44.0	22
Su 25b	18.1	6.9	NA	500.0	NA	230.0	250.0	NA	NA	185	118	135	122	109	61.0	NA
Su 25c	NA	NA	NA	15.0	NA	110.0	NA	NA	NA	220	195	126	98	96	NA	NA
Su 25d	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	180	NA	136	113	47.0	NA
Su 25 mean	18.7	8.1	73.0	288.0	NA	227.0	225.0	80	NA	192	155	137	129	107	51.0	22
Su 50a	4.6	5.8	2.4	6.5	5.6	10.6	10.6	NA	79	240	30	NA	59	54	29.0	NA
Su 50b	0.0	NA	NA	NA	NA	NA	NA	NA	83	NA	NA	NA	NA	NA	NA	NA
Su 50 mean	4.6	5.8	2.4	6.5	5.6	10.6	10.6	NA	81	240	30	0	59	54	29.0	NA
Su 75a	0.9	4.6	1.5	1.3	1.0	1.1	1.1	NA	250	50	67	151	99	30	15.6	NA
Su 75b	4.3	NA	102.0	290.0	210.0	175.0	180.0	NA	NA	NA	102	29	37	92	56.0	NA
Su 75 mean	2.6	4.6	51.7	146.0	105.0	88.0	90.0	NA	250	50	84	90	68	61	35.8	NA

Key
NA No water collected

Concentrations given as µg/l

4.3.6 Isoproturon in mole drainage water

Three mole drains, 25, 24 and 22 contained 75 ml capacity sumps from which water was collected on a routine basis. It would be difficult to establish whether the drainage water collected in the sump reflected the initial drainage water, the penultimate drainage water or an average of the two. Comparison with the field drain isoproturon concentrations for 50 d would suggest that the water in the sump reflects the 'tail' of the event. Water was collected from all three sumps on days 50, 56 and 64, with concentrations of 185 to 290 μg/l on day 50 to 108 to 129 μg/l on day 64 (see Figure 13 and Table 8). It is interesting to note that the mole with the highest concentration of pesticide varied depending on the event. Water could be collected from only one or two of the three moles from days 75 to 90, and none subsequently. The reduction in water reaching the mole drains (and also the field drain) from day 75 onwards can be ascribed to an increasing water deficit in the soil, influenced mainly by crop water use and evaporation. It is interesting to note the similarity in pesticide concentrations in overland flow and mole drain water from the day 75 period. Soil surface residues also remained stable over this period, at around 1 mg/kg.

Table 8 *Isoproturon and anions in mole drain water*

Days after isoproturon	50	56	64	75	78	90
Mole 25 isoproturon (ppb)	280.0	134.0	108.00	67.0	65.00	44.0
bromide (ppm)	13.6	6.0	3.10	2.7	3.00	4.0
chloride (ppm)	18.0	24.0	14.50	21.0	21.00	5.5
sulphate (ppm)	32.0	33.0	23.00	29.0	22.00	16.5
nitrate (ppm)	208.0	>100.0	>50.00	36.0	0.20	>50.0
Mole 24 isoproturon (ppb)	290.0	205.0	124.00	NA	NA	NA
bromide (ppm)	1.0	0.4	0.05	NA	NA	NA
chloride (ppm)	14.0	13.0	4.50	NA	NA	NA
sulphate (ppm)	29.0	26.0	16.00	NA	NA	NA
nitrate (ppm)	>50.0	>25.0	>25.00	NA	NA	NA
Mole 22 isoproturon (ppb)	185.0	210.0	129.00	NA	36.00	NA
bromide (ppm)	0.1	0.1	0.05	NA	0.05	NA
chloride (ppm)	13.0	8.5	5.50	NA	8.00	NA
sulphate (ppm)	26.0	17.0	12.00	NA	17.50	NA
nitrate (ppm)	>50.0	>25.0	>25.00	NA	21.00	NA

Key
>50.0 Above highest standard
NA No water collected

4.3.7 Isoproturon in main field drainage water

The first rainfall event which triggered the autosampler is shown in Figure 12 and the second in Figure 15. A number of observations can be made from these storm events:

- In both events the delay between the onset of rainfall and drainflow appeared to be related to the development of a positive head in the topsoil recorded by the 10 cm PTT (Figure 16), as described in section 4.1.2.

- Isoproturon and drain flow velocity appear to be closely related, although the peak pesticide concentration lags behind peak drainflow by 1 h and pesticide concentrations decline more slowly with time with respect to drainflow. This hysteresis effect can be seen for both storm effects in Figure 26. Possible explanations are given below.

- Isoproturon concentrations and anion concentrations show an inverse relationship in both storm events (see Figures 27 and 28). In other words as isoproturon concentrations increase, so anion concentrations decrease, and vice versa.

The main field drain catchment for the plot was estimated to be 1800 m^2 and together with the amount of pesticide known to be available in the soil surface at that time (2.9 mg/kg, giving approximately 167 g in 1800 m^2), in 8 h of rainfall on 1,4,93 drain efflux was 7000 l. A cumulative loss of 2.5 g is suggested, this would mean a loss of 1.5% to the drainage in the first event. The second event based on the same parameters yielded 2 g, an equivalent of 1.2%. Therefore in the combined events, 2.7% of the pesticide was lost to the drainage in a matter of 3 days. It was estimated that 30% of the rainfall that fell in the events entered the tile drain.

4.3.8 Isoproturon in the ditch at the bottom of the field

Water samples were taken on a routine basis (once a week on average) both from the field drain 2 outfall and from the ditch 1 m upstream from the field drain 3 outfall. Unfortunately the field and adjacent ditch at Wytham do not comprise a hydrologically defined catchment. A component of the water in the ditch would have come from the nearby Wytham wood and therefore would have diluted the field/pesticide component, but the figures are of interest in terms of revealing pesticide concentrations in a ditch which ultimately enters the Thames.

Pesticide concentrations in the ditch from the spraying day until 100 days after spraying were routinely above 0.1 μg/l (see Figure 29 and Table 9). The highest concentrations of 16.8 and 23 μg/l corresponded to rainfall events on or prior to days 42 and 50.

4.4. MODELLING WORK

Only a very preliminary attempt has been made to model the Wytham soil water processes. At this point in time it is not certain that the processes controlling pesticide runoff have been defined and a suitable conceptual model formulated. The model developed to describe pesticide movement at Rosemaund (Williams and Volkner, 1993) has been modified in a first attempt to simulate the perceived Wytham soil flow routes.

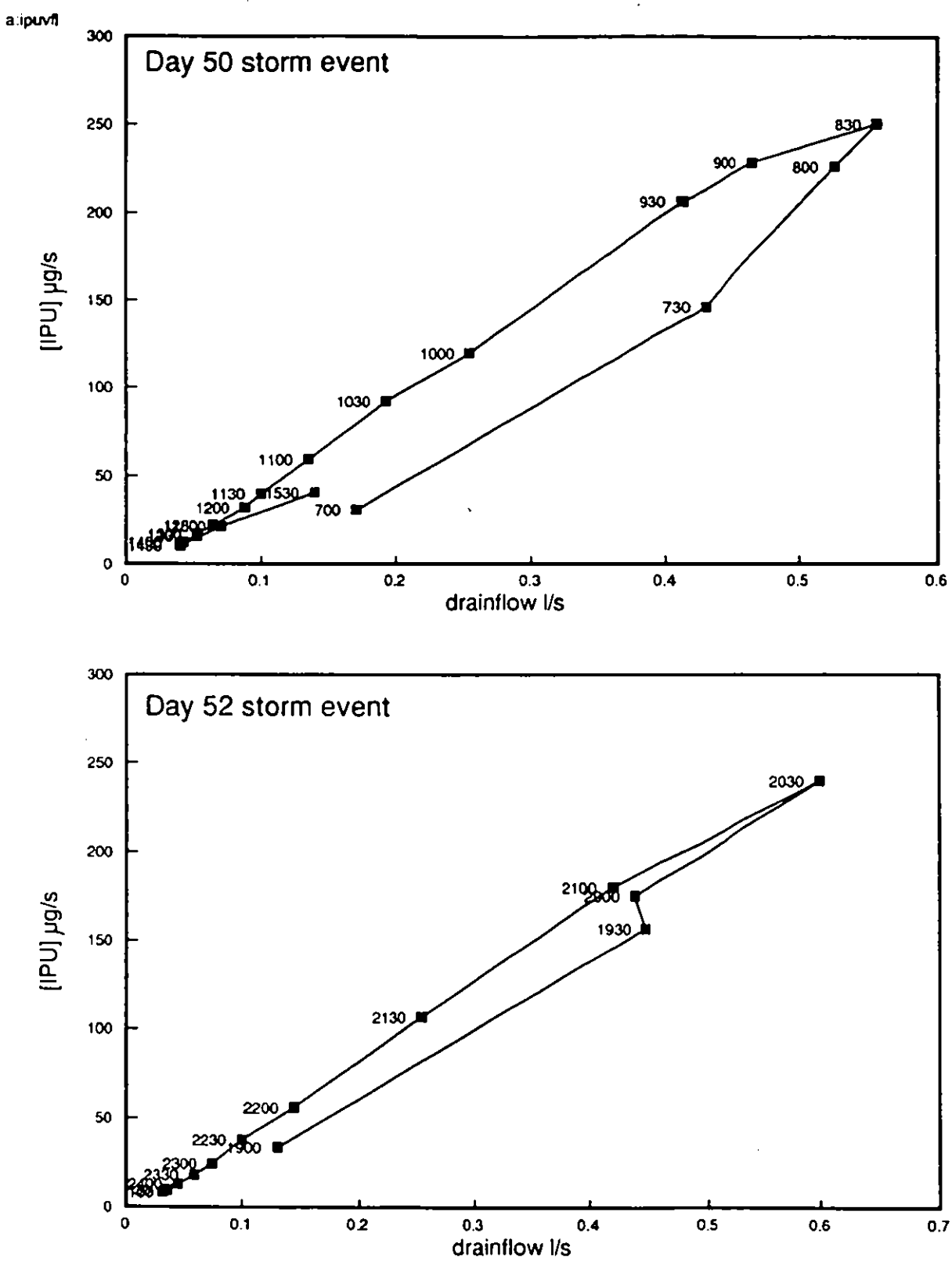


Figure 26. Comparison of isoproturon concentration with drainflow

a:50dsaltb

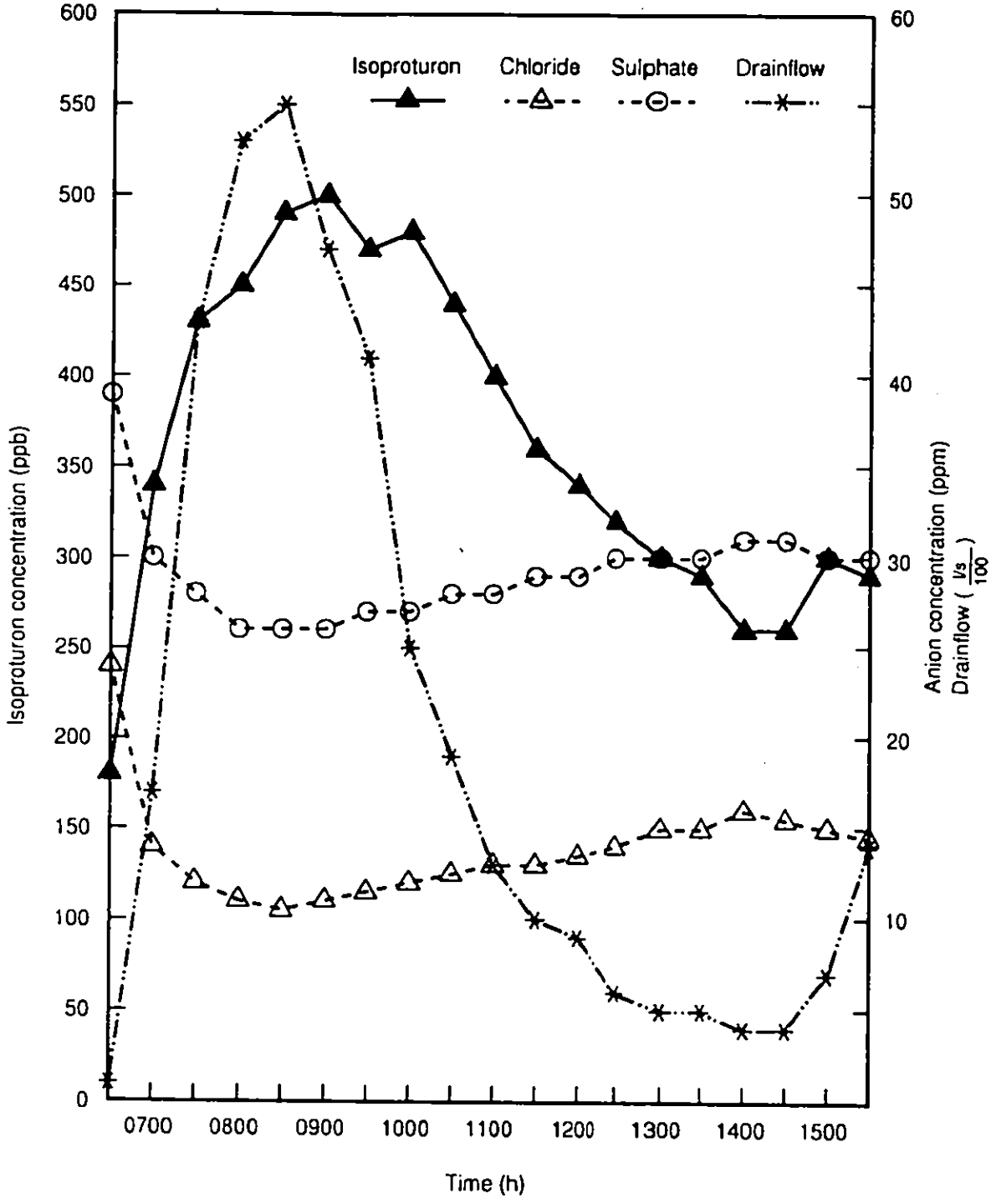


Figure 27. Comparison of solute concentrations with drainflow for the 50 d storm event

a:52dsaltb

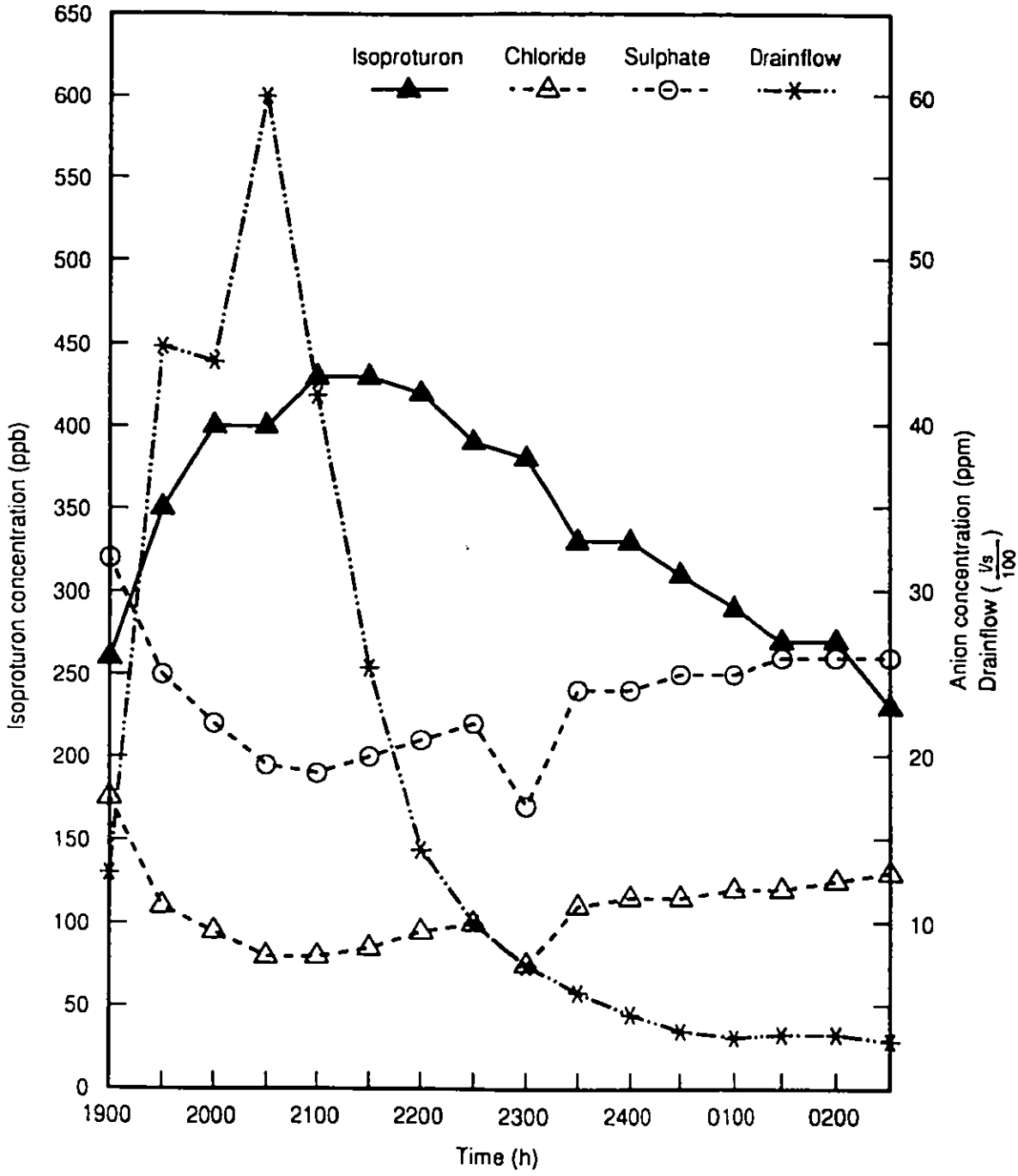


Figure 28. Comparison of solute concentrations with drainflow for the 52 d storm event

a:ditch

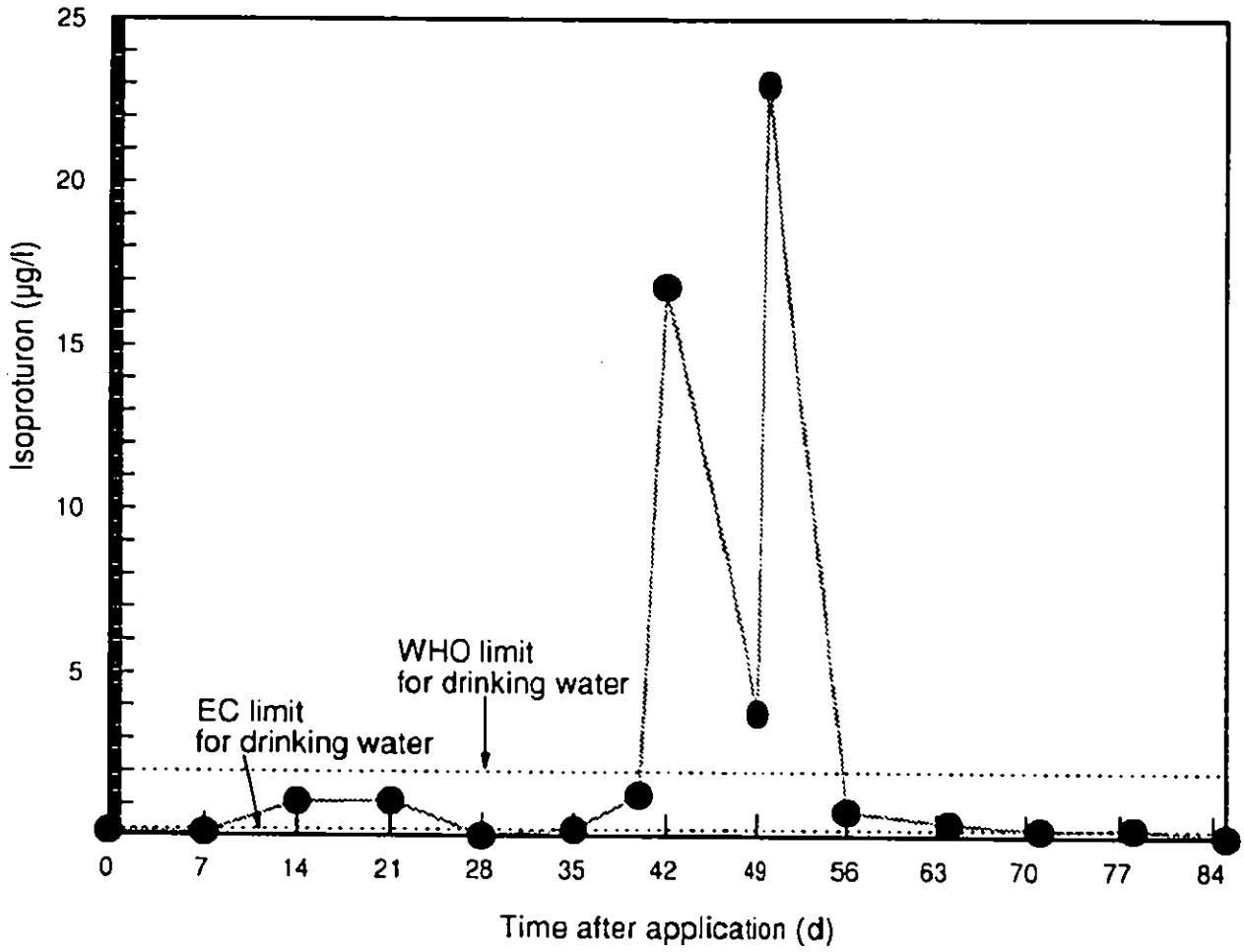


Figure 29. Isoproturon concentrations in water samples taken during routine sampling from the ditch at Wytham

Table 9 *Isoproturon and anions in ditch and field drain 2 outfall water*

Days from isoproturon application	-69	0	7	14	21	28	35	40	42	49	50	56	64	71	78	85	100	113
Ditch isoproturon (ppb)	(0.1)	0.16	0.15	1.10	1.12	(0.08)	0.25	1.31	16.80	3.8	23	0.81	0.43	0.24	0.28	(0.08)	0.14	(0.10)
Ditch chloride (ppb)	ND	ND	ND	ND	ND	ND	ND	ND	33.00	31.0	24	30.00	27.00	28.00	28.00	29.00	28.00	31.00
Ditch sulphate (ppm)	ND	ND	ND	ND	ND	ND	ND	ND	>50.00	>50.00	>50.00	>50.00	>50.00	>50.00	>50.00	84.00	>50.00	>50.00
Ditch nitrate (ppm)	ND	ND	ND	ND	ND	ND	ND	ND	7.00	11.0	>25	10.40	10.00	8.80	6.40	6.40	4.20	4.20
FD2o isoproturon (ppm)	(0.1)	0.18	1.53	1.16	0.80	0.95	(0.08)	26.00	0.32	122.0	NA	2.10	0.83	0.86	0.99	0.38	0.92	0.09
FD2o chloride (ppm)	ND	ND	ND	ND	ND	ND	ND	28.00	32.00	23.0	NA	28.00	25.00	26.00	26.00	27.00	24.00	29.00
FD2o sulphate (ppm)	ND	ND	ND	ND	ND	ND	ND	50.00	>50.00	>50.00	NA	>50.00	>50.00	>50.00	>50.00	74.00	>50.00	>50.00
FD2o nitrate (ppm)	ND	ND	ND	ND	ND	ND	ND	9.20	1.60	>25	NA	6.60	4.40	2.40	3.00	1.60	9.00	1.40

Key

ND	No determination made
NA	No determination possible
>50.00	Above highest standard
(0.10)	Below detection limit

Note for isoproturon: EC limit for drinking water is 0.1 ppb
WHO limit for drinking water is 2 ppb

The model consists of a number of connected boxes which describe the changing properties of the soil both vertically through the soil profile and horizontally as they are influenced by the presence of drains. Macropore flow is allowed through cracks that penetrate through the soil layers and whose extent is defined by the percentage of volume the macropores occupy. Cracks close as the soil water content increases in a linear manner up to a minimum value which represents the volume of biopores. The model is designed to represent a drainage element of the soil which is considered as the area from one drain mid point to the next. For this exercise the mole drains were considered to be the relevant drainage mechanism. The model is driven by hourly rainfall with the rate of movement of water out of a given box being proportional to its water content.

Pesticide is distributed between the soil and the soil water using a single valued instantaneous adsorption isotherm. The partition coefficient was calculated from the product of the koc and the organic carbon content. Degradation of pesticide occurs at a uniform rate throughout the profile, the rate being proportional to the pesticide concentration. Pesticide is transported through the soil profile dissolved in the soil water.

The model was set up so that the main flow path was lateral through the near surface (to 40 cm), this flow being intercepted by a high conductivity area representing the mole drains. Once in the mole the water was transported immediately to the tile drain. Water was not able to move vertically other than in the area immediately above the drain. Lateral flow below 40 cm was also not allowed.

A preliminary simulation of the first two rainfall event described earlier was carried out with no site calibration other than to establish the flow paths described above. The results achieved were encouraging, with the model predicting concentrations in the drains of a few hundred μg/l for both events; the first higher than the second. It is too early to say whether this modelling approach has been valid or useful in describing the pesticide processes at Wytham, however, it is heartening that such high concentrations as those observed at Wytham can be simulated.

5. Preliminary conclusions on pesticide persistence and transport at the field site

5.1 DEGRADATION

The degradation of isoproturon as deduced from the reduction in concentration in the soil surface was as expected. A DT_{50} of 30 d was estimated from the decline in residues. The increased persistence of residues from 78 d after application suggests that these residues may have an enhanced protection from biodegradation. This may be due to a strong sorption with the organic matter fraction of the soil. However, rainfall during the 80-162 d period did elicit small-scale overland flow which contained isoproturon in the range of 13-60 μg/l. Clearly the pesticide does not become completely unextractable so why does the degradation rate 80 d after application decline to an approximate DT_{50} of 70 d from an initial value of 30 d? Walker (personal communication) has shown with alachlor that the proportion of aqueous

Table 10 *Isoproturon present in top 2 cm of soil at Wytham (mg/kg)*

Days after isoproturon spraying	7	21	35	49	64	78	100	113	127	141	155
Replicates											
1	7.80	6.96	2.29	2.91	1.85	0.83	0.92	0.89	1.02	0.41	0.37
2	8.24	6.82	2.02	2.95	1.78	0.86	1.26	0.84	1.06	0.57	0.50
3	9.69	7.60	2.76	2.92	2.35	1.13	0.91	0.79	0.77		
4	10.43	8.50	2.98	2.82	2.35	0.94		0.69	0.80		

available pesticide as opposed to total declines with time. Degradation must therefore become increasingly limited by desorption kinetics over time. An alternative explanation is a decline in microbial activity due to a reduced moisture content in the soil surface, an important factor in degradation rate (Walker, 1991).

5.2 THE RELATIONSHIP BETWEEN SOIL RESIDUES AND THE PESTICIDE AVAILABLE FOR TRANSPORT

The mechanism of pesticide transport to the drains via macropores studied by this project, is based on the assumption that the majority of water entering the macropores is from the immediate soil surface. In this case the pesticide in the top few cm of the soil (mixing zone) is that which is primarily responsible for contamination of the drainage water. The pesticide in the soil may be considered as belonging to one of three groups: aqueous, weakly sorbed (aqueous extractable) and strongly sorbed (methanol extractable). Sorption experiments for isoproturon and Wytham soil have not yet been carried out, so it cannot yet be predicted how much of the pesticide belongs to each category in the field. However by day 50 the aqueous phase is likely to be by far the smallest component. It may be that only the aqueous phase pesticide is involved in transport in the storm events. This pool would appear to be replenished between the events by desorption from the solid phase. It is not clear whether desorption occurs on a significant scale during a storm event (Note: pesticide may also be transported whilst sorbed onto sediments).

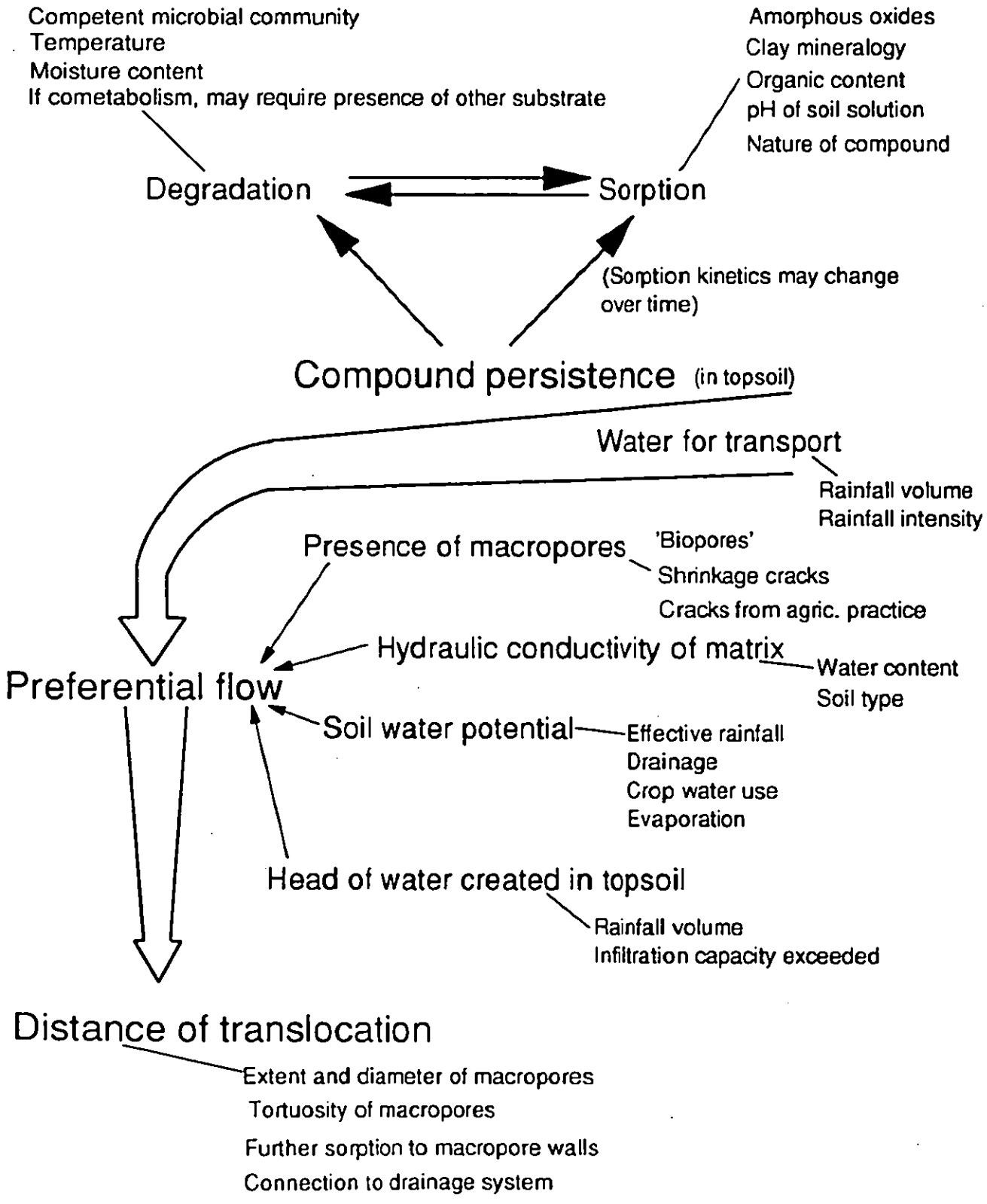
The amount of rainwater mixing with soil water at the soil surface (once matrix infiltration capacity had been exceeded) must also influence the concentration of pesticides found in drainage water (probably related to rainfall intensity). This will dilute the pesticide concentration of the original soil porewater. A schematic diagram which illustrates some of these factors is shown in Figure 30.

5.3. SUGGESTED MECHANISM FOR PESTICIDE TRANSPORT TO DRAINAGE

Data shown in Figures 27 and 28 together with soil hydrology data (Figure 16) may be interpreted in the following way:

a:concept1

Figure 30. Factors involved in pesticide transport by vertical by-pass flow



(1) Prior to rainfall the majority of pesticide is distributed throughout the top few cm of the soil, whilst the anions are distributed throughout all of the topsoil, as natural components of the soil porewater, possibly anions may also be concentrated on some of the macropore walls due to water evaporation (Figure 31).

(2) Rainfall wets up the topsoil from the top down, nothing happens until a positive head is achieved in the topsoil (top 10 cm). Some of the pesticide may be moved to below the surface 'mixing zone' during this period. In this case the longer the delay between inception of rainfall and initiation of drainflow, the less pesticide may be available for transport by preferential flow mechanisms (Baldwin *et al.*, 1975).

(3a) When the topsoil becomes saturated and cannot accept any more rainwater, lateral water movement is initiated, possibly both within the top 10 cm and at the soil surface. Some of this water connects to vertical macropores.

From experimental work on mole drain flow and solute movement at Wytham, Haigh (1985) suggested that water entered the macropores in the B horizon from within the topsoil, rather than directly from the soil surface.

(3b) The macropore walls become saturated as water moves down from the surface.

(3c) Water runs down a combination of macropores to reach the drains, and re-adsorption of pesticide onto worm burrow walls may occur (Edwards, 1991; Stehouwer *et al.*, 1993). The function of the macropores to transport water may be inhibited by trapped air unable to escape and thus prevent further water entry. Water and pesticide are now moving from the soil surface to the drains, driven only by the positive head of water generated by the rainfall, subsequent to topsoil saturation having been achieved. The first water to arrive at the drains may (a) flush out old soil water in the profile, (b) transport salts from the macropore walls, or (c) mix thoroughly with mobile soil water (with a high salt concentration) in the upper horizon (Haigh, 1985).

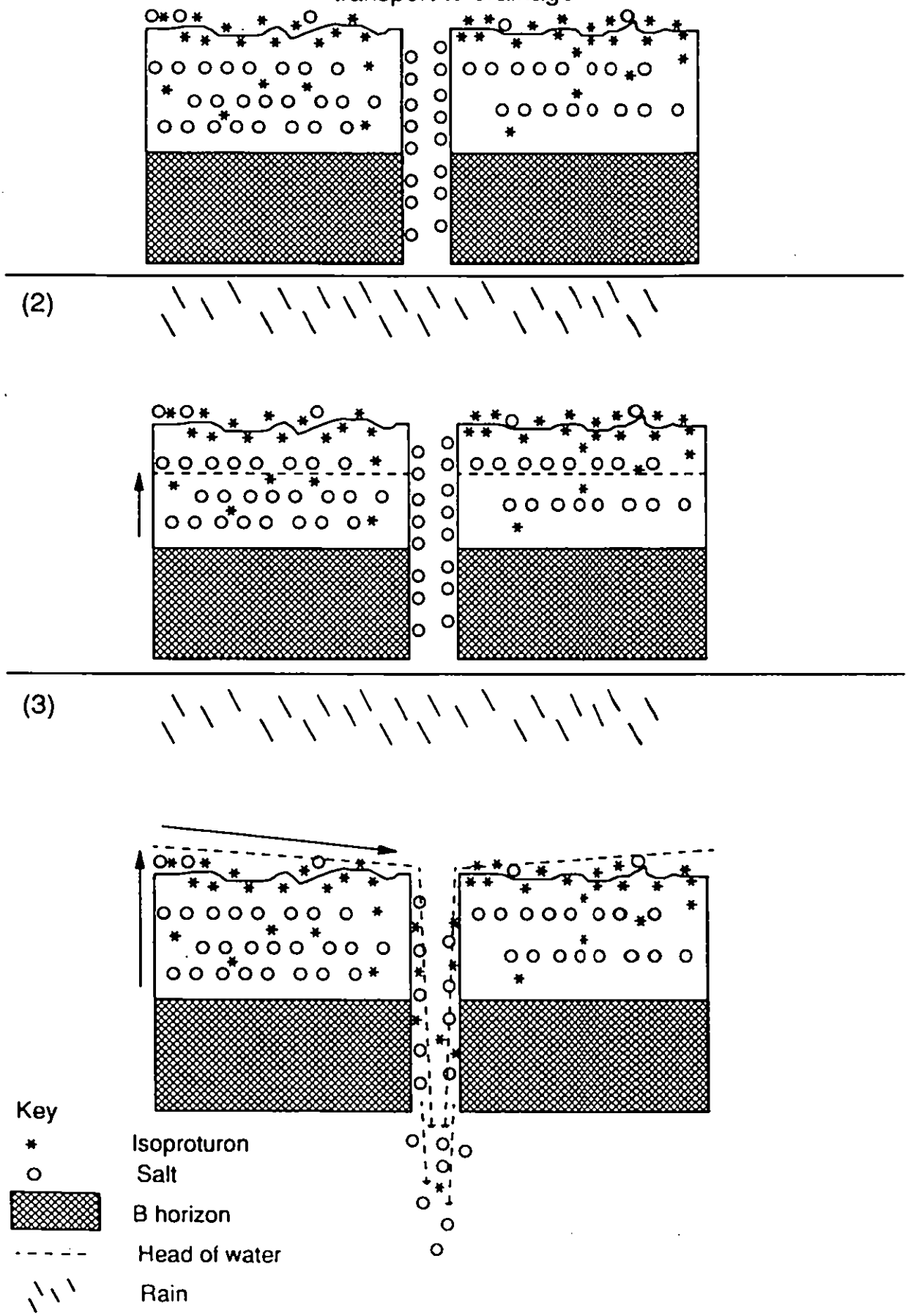
(4a) As more water arrives from the soil surface, where the majority of pesticide is concentrated, so the pesticide concentration rises. The anion concentrations decline (possibly to the same concentration of the rainwater/overland flow water).

(4b) Subsequent rainfall events during the drainflow period are rapidly translated to changes in drainflow velocity and higher pesticide concentrations. Pesticide concentration may, however, be reduced due to depletion of the available pool during the event.

(4c) Overland flow must occur at least to a limited extent to feed the macropores, whilst significant overland flow probably also occurs during the rainfall period and takes pesticide off the plot, as water was collected from the overland flow traps during this period. It is believed that the overland flow meter was not working correctly over this period.

(4d) Lateral interflow is also likely to occur within the saturated soil at the top 10 cm, although no water sampler was in place to confirm this. Lateral movement of bromide tracer from mole 25 to mole 24 may be an indication of lateral interflow (see Table 2).

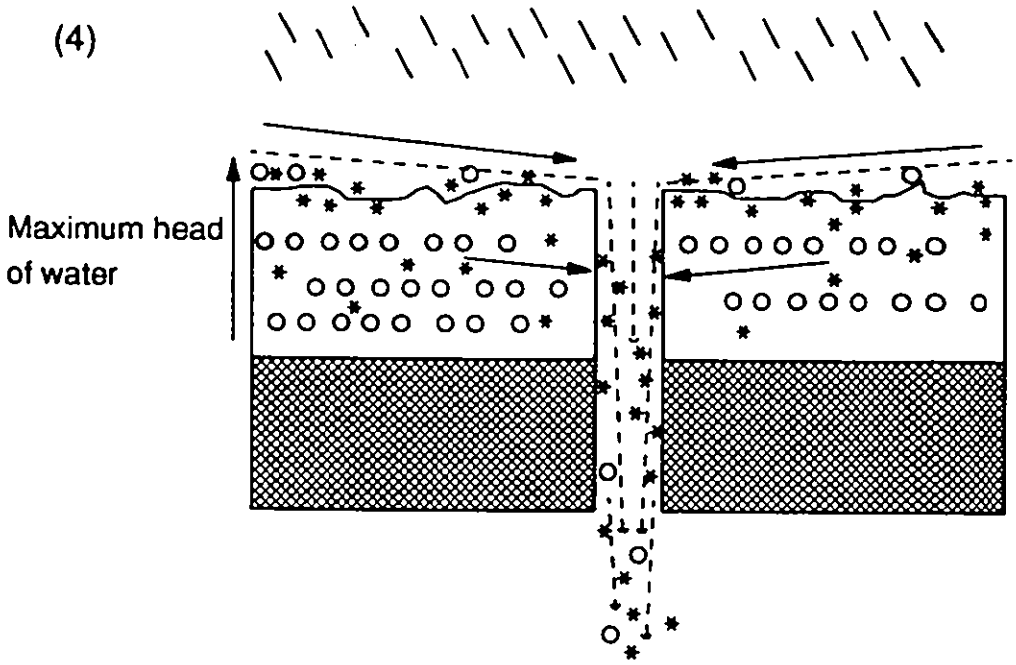
(1) a:saltcon1 Figure 31. Suggested mechanism for pesticide and salt transport to drainage



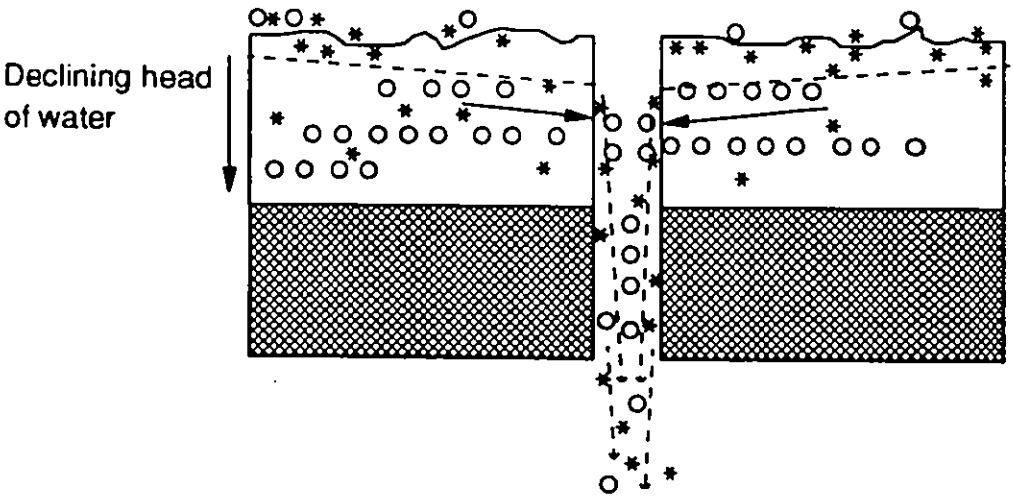
a:saltcon2

Figure 31. continued

(4)



(5)



Key

- Isoproturon
- Sulphate and chloride
- B horizon
- Head of water
- Rain

(5) As drainflow declines, the proportion of water arriving directly from the soil surface (with high pesticide concentration) is reduced, but water continues to arrive laterally through the topsoil, bringing water with a higher salt and lower pesticide concentration.

Therefore, data from these storm events suggest that changes in pesticide and anion concentrations may be attributed to the different origins of the water entering the drains.

I) Some water may have entered from the soil surface with a steady pesticide concentration, of perhaps 600 μg/l, and low anion concentrations similar to that found in overland flow water (see Figure 32)

II) Other water may have moved into the macropores from a lateral direction from 10 cm and above. It may have contained little or no pesticide (not having penetrated to this depth in appreciable quantities) but an anion concentration similar to that found in the suction samplers (see Figure 32). This water was possibly the last to start entering the macropores and the last to stop, although Haigh (1985) suggested that lateral water movement into macropores in the B horizon was the major component throughout a drainflow event.

Initially, water may first flow down from the soil surface and lose pesticide by readsorption on the macropore walls whilst salts on the macropore walls go into solution (thus raising the salt concentration). Then water from the soil surface becomes the dominant component of drainwater, with a high pesticide and low salt concentration. Towards the end of the event as drainflow decreases, water entering the vertical macropores from lateral macropores within the 'A' horizon may become an important component, introducing water with a higher salt and a lower pesticide concentration then that from the soil surface. A variation on this theory is provided by Haigh (1985), who suggested that the relationship between anion concentrations in the drainwater was related to increases and decreases in mixing of rainwater (input water) and a mobile soil water component within the A horizon. Thus during low flow periods the maximum mixing occurs between the new and old water in the A horizon.

In Figure 26 a hysteresis effect can be observed. Pesticide concentration was found to lag slightly behind the peak drainflow, such that for any given drainflow velocity the pesticide present was greater as drainflow was decreasing rather than increasing. In other words less pesticide was carried at the beginning of the rainfall event than at the end. There are a number of possible explanations:

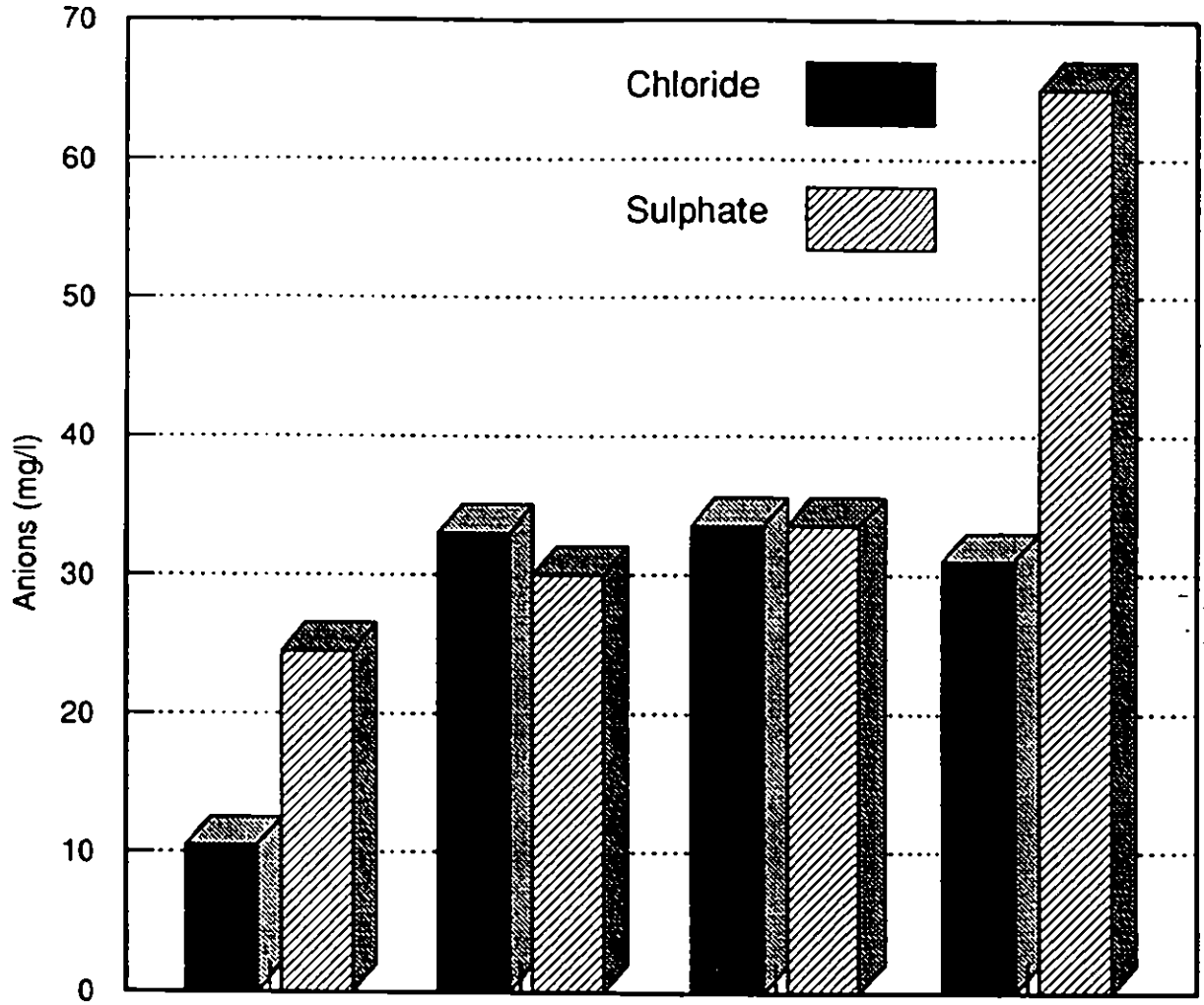
- Readsorption of pesticide on macropore walls in the initial phase of the event. Once this capacity has been satisfied, less of the pesticide travelling down to the drains is retained.

- Increasing mixing and transport of pesticide at the soil surface.

- The changing ratio of old water to new water (rainfall) ie initally drainwater is largely old soil porewater. Rainfall interacting with the surface soil becomes a larger and larger component until the ratio declines as rainfall stops and more old water comes in again.

It seems probable that the mole drain network, ie artificial drainage, is the main culprit in contamination of the nearby surface water. Whether water enters the mole drain primarily via a combination of 'the slot' left by their manufacture and biopores, or by biopores only,

a:anion50d



Source of sample	OFT	Su 25	Su 50	Su 75
Chloride	10.5	33.0	33.5	31.0
Sulphate	24.5	30.0	33.5	65.0

Figure 32. Comparison of anion concentrations found in water samples taken from the overland flow traps and the 25, 50 and 75 cm suction samplers 50 days after isoproturon application (mean of 2-4 observations)

has yet to be established. Lateral interflow and overland flow also occur, but their effect on direct contamination of the ditch is less clear. Bromide tracer evidence suggests that water can move across the 'inter-mole area' either above or below the surface. Figure 30 lists the main factors which are believed to influence pesticide transport by vertical by-pass flow. An opportunity to test the theories described above, and to see whether the same phenomena are repeated should arise in the 1993-94 season.

The evidence, therefore, from the first season of fieldwork at Wytham, suggests that a mole drained heavy clay soil poses a serious threat in terms of pesticide contamination to the surrounding water courses. The results so far demonstrate that high contamination of drainage water can occur for a considerable period after pesticide application to the field.

6. Future work

6.1 FIELD EXPERIMENTATION

A hydrologically defined plot will be constructed in which the proportion of rainwater and pesticide in overland flow, lateral interflow and drainflow can be calculated (see Figure 33). It is not possible to quantify movement of water to below drain depth in the field, but this component is not thought to be large, based on this year's tensiometer data. Through the employment of additional pressure transducer tensiometers, flow meters with data loggers and autosamplers, it is hoped to build a more complete picture of water and pesticide movements through the soil during a storm event.

6.2 LABORATORY EXPERIMENTATION

The soil profile and characteristics will be described in greater detail. SSLRC will describe the soil profile in physical terms, including particle size analysis. HRI will study the aerobic degradation potential of the different soil depths, as well as adsorption potential studies for isoproturon. If the appropriate equipment is available, IH will study anaerobic degradation potentials at different soil depths.

Both repacked soil columns and undisturbed soil columns containing soil from Wytham will be used to study macropore transport of solutes. A number of parameters will be manipulated, including irrigation rate, position of tracers in the column, and the presence of macropores. In essence, the columns will be used to verify suppositions on macropore flow which come from interpretations of field data.

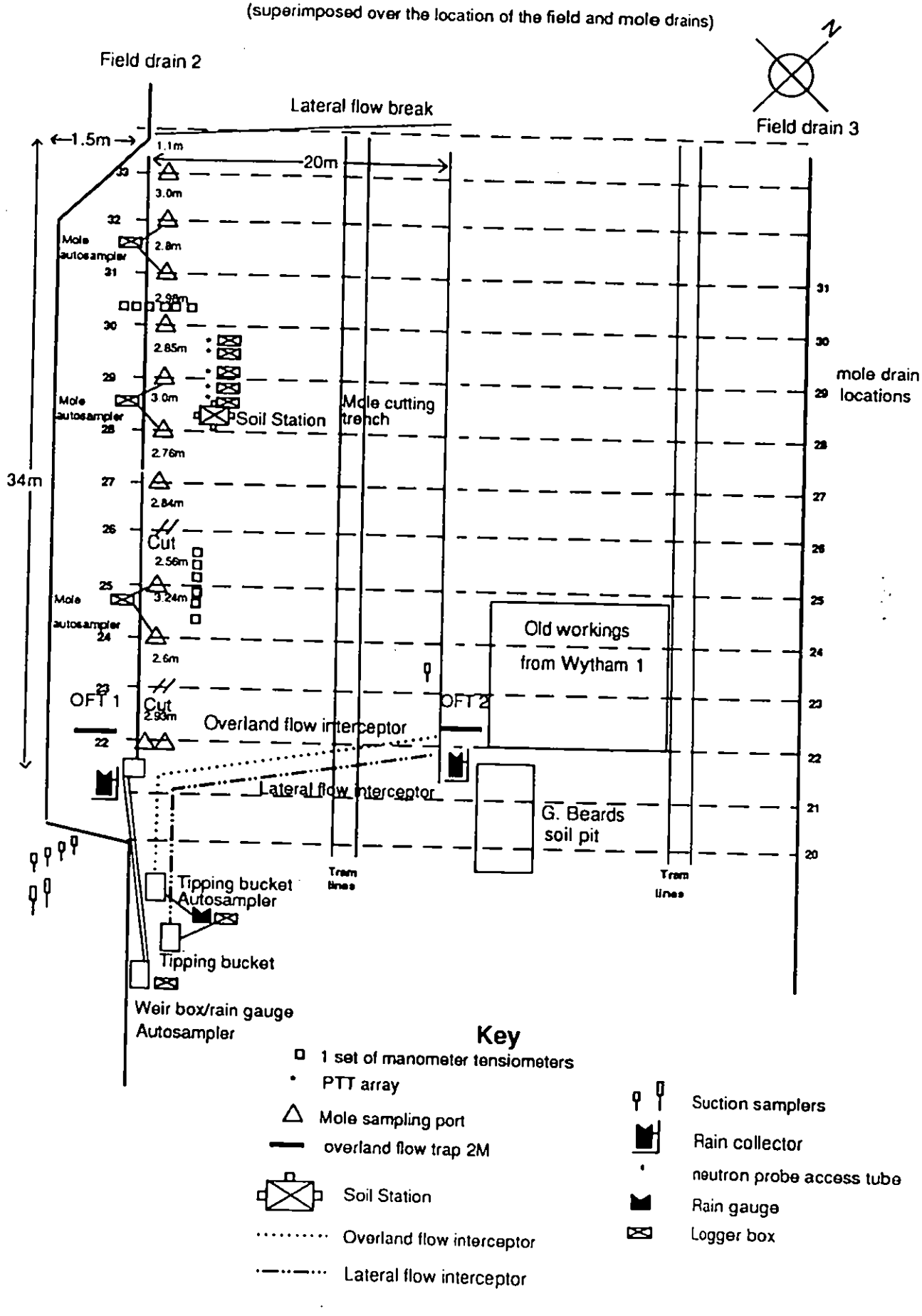
6.3 MODELLING STUDIES

The data collected from Wytham in the first year confirm the importance of by-pass flow in heavy clay soils. Thus models of flow, and the transport of solutes through systems that are controlled by Darcian flow through the matrix, are not appropriate. Attempts to model the system at Wytham will concentrate on developing modules that describe by-pass flow and its

a:newwyt3b

Figure 33. Wytham location of instruments

(superimposed over the location of the field and mole drains)



link with the matrix. The following processes are likely to be of key importance in such a model:

i) The commencement and cessation of by-pass flow. This can be controlled either by the conditions in the soil matrix or by rainfall intensity.

ii) The interaction between by-pass flow and the matrix. Here the depth of penetration of by-pass flow must be considered, especially as it is controlled by the dryness of deeper soil layers. Additionally, the interaction of solute in the by-pass flow with the matrix will have implications for sorption/desorption.

iii) The nature of the by-pass flow routes will change with time e.g. shrink/swell cracks will change diameter with water content.

iv) The connectivity of the by-pass flow routes will obviously influence the depth and speed of movement of water and solutes by-passing the matrix.

The development of conceptual models to describe this processes will be undertaken as follows:

a) The literature will be reviewed with respect to modelling of by-pass flow carried out by other workers. There has been a great deal written concerning the flow of water in by-pass flow routes, but little on the movement of solutes.

b) The interaction between the matrix and the by-pass flow route will be considered in a simplified form, a single macro-pore passing through an homogeneous matrix. This situation can be set up in the laboratory under controlled conditions and thus generate vital information for the conceptualization of this system.

c) Through b) above, several types of by-pass flow route can be investigated i.e. structural cracks, earthworm channels and shrink swell cracks.

The aim is to develop a model of a simplified system so as to isolate individual or small groups of processes within the system. The expansion of the model to a field scale will need much thought, particulary with regard to the distribution and connectivity of macropores.

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Annex A Pesticide transport literature review

A 1 HYDROLOGICAL PROCESSES IN CRACKING CLAY SOILS

One of the challenges to environmental scientists is still to determine by what routes the escaping '1 %' is lost from clay soils. Pesticide may be transported in solution, co-transported with other organics, or bound to sediment particles (Ghodrati and Jury, 1992) depending on the sorption coefficient of the pesticide, and type of indigenous organic compounds (Leonard, 1990).

Four different types of water movement in clay soils can be identified:

A 1.1 Infiltration into the matrix.

Occurrence:
Predominant in dry spring and summer periods, when rainwater fills micropores in the soil matrix from which water has been lost by evaporation and crop uptake. Once the infiltration capacity has been satisfied, preferential flow will occur. The hydraulic conductivity of the saturated matrix is seen as extremely low. It has also been noted that cracked dry clay soils have an initially reduced hydraulic conductivity, exhibiting almost hydrophobic characteristics which will also promote preferential flow during intense rainfall.

A 1.2 Vertical bypass flow

Occurrence:
When the infiltration capacity of the matrix is exceeded or when rainfall intensity exceeds the matrix infiltration acceptance rate (White *et al.*, 1986; Radulovich *et al.*, 1992)

Transport routes
Cracks induced by soil shrinkage from evaporation or those induced by agricultural activity such as mole draining (Harris *et al.*, 1984). Biopores which include worm burrows and root holes.

Research
As vertical macropores appear to represent the principal route whereby pesticides can enter the subsurface drainage system or groundwater, they have received considerable attention. Prior to macropores transporting water, surface ponding of rainwater must occur (it is plausible that localised perched water tables may feed macropores below the soil surface). In these situations the rainwater that has not been accepted by the matrix runs over the surface, looking for an escape. This ponded mobile water is believed to interact with the top cm or so of the soil surface, the so called mixing zone (Ahuja and Lehman, 1983), whose thickness will vary with the surface structure of the soil. This mixing zone is of great significance with respect to clay soils, as the great majority of the pesticide remains in the top soil surface, sorbed onto soil particles or in the soil solution. Therefore the rainwater prior to moving into macropores will be running through the 'pesticide rich' part of the soil. The principal reason for the pesticide remaining in the top few cm of the soil surface is due to adsorption reactions with organic matter. This is in contrast to other solutes such as halides

(Fermanich and Daniel, 1991).

In late spring and summer shrinkage cracks are the principal macropore component, Kneale and White (1984) estimated 10-20% of rainfall in dry periods bypassed the top 9 cm via this route. The amount of water leached via shrinkage cracks decreases with time during prolonged rainfall events as the clay soil begins to swell, and the cracks close (White *et al.*, 1986). Pesticide contamination of water courses in these conditions, however, may not be serious as with a low water table drain flow is rarely initiated. Deep penetration of pesticides into the soil matrix may present a longer term problem, due to low degradation and sorption potentials at depth (Pothuluri *et al.*, 1990). The pesticides may persist and become mobilised when the water table rises in the winter.

In the wetter conditions of the autumn and winter, vertical worm burrows represent the principle macropores available to rainwater. Vertical worm burrows are formed by detritivores, the worm population that feeds or collects organic matter at the soil surface which is then ingested within the confines of the burrow (Lee, 1985). The most well known of these worms is *Lumbricus terrestris*. The number of these organisms is much reduced in fields under arable cultivation compared with pastures. Studies have shown that only a small number of the available worm burrows actually transport water during a preferential flow event. Trojan and Linden (1992) correlated volumes of water transported to the topographical aspect of the worm openings, with worm burrow openings on ridges transporting less water than those in depressions. Worm casts or the worms themselves may block the openings (Ela *et al* 1992) and of course very few of the worm burrows are continuous in terms of reaching groundwater depth or intersecting field drains. In addition, worm burrows may not transport rainwater throughout a rain event due to the formation of surface seals or plugs by sediment (Bouma and Anderson, 1977; Ela *et al*, 1992). At the beginning of a rain event rainwater may initially only run down the walls of a worm burrow rather than filling the whole pore (Radulovich *et al.*, 1992) and run at comparatively low flow velocities (Bevan and German, 1982). This may give opportunities for readsorption of the pesticide on burrow walls which have a higher TOC than the surrounding soil matrix, particularly with increasing depth (Stehouwer *et al.*, 1993). Edwards (1991) suggested this may be why less pesticide leached out of worm burrows compared with artificial macropores in his experiments. It can be assumed that once the burrow is completely full of water and the water is being transported at higher velocities (up to 6 cm s^{-1}, Bevan and German, 1982) the opportunities for significant adsorption are much reduced.

Contamination significance

In the critical autumn and early winter period in which winter cereals are sown and herbicides applied, vertical bypass flow, particularly via worm burrows, is seen to represent the principal loss route. Water moving via lateral interflow may enter vertical macropores and then be transported to the field drainage system. Another possibility is that worm burrows which open at footslope areas which have received additional deposits of pesticide after overland flow can transport above average concentrations of pesticide in subsequent rainfall events.

A 1.3 Lateral bypass flow or interflow

Occurrence

This will only occur in saturated conditions in fields containing a gradient and a subsurface boundary layer of a lower hydraulic conductivity than the upper horizon.

Transport routes
This type of water movement may utilise structural cracks or biopores, predominantly laterally aligned worm burrows and in certain circumstances possibly along buried straw stalks.

Research
Of the three preferential flow routes lateral interflow seems to have received the least attention. It is difficult to study outside the field environment and methods to study it within the field are faced with the difficulty of assessing whether an interceptor trench may act as a sink, and so create artificial interflow. A likely transport route would be along horizontal worm burrows formed by sub-surface foraging (geophagus) worms (Lee, 1985). Harris *et al.* (1984) related a plough pan to a perched water table and lateral interflow at Brimstone. Results from Brimstone suggested that whilst lateral interflow accounted for 15% of the rainfall, only insignificant amounts of the pesticides under study were involved.

Contamination significance
The significance of lateral interflow in terms of pesticide contamination may be :

- In feeding vertical macropores below the soil surface which connect to the field drainage system.
- In conducting pesticide down the slope to the riparian zone, and from there into drainage ditches.
- In conducting pesticide down the slope to an area of the field with a more conductive soil type, where it percolates down to groundwater.

A 1.4 Overland flow or surface runoff

Occurrence
This will be the same as for vertical bypass flow. Overland flow may be seen as a two-stage process involving small short-range movement, and large-scale overland flow or sheet flow. The short-range overland flow is drained away by macropores and when this capacity is exceeded the short range overland flow movements coalesce to form sheet flow.

Transport routes
This occurs over the soil surface and within the top soil to a 1-2cm depth mixing zone. When not drained away by macropores, rivulets form in natural depressions or wheel tracks left by agricultural machinery, allowing rapid transport over long distances.

Research
Harris *et al.* (1984) estimated that 4-11% of rainfall at Brimstone over the winter could be accounted for by overland flow. Ahuja and Lehman (1983) simulated overland flow in the laboratory using soil boxes and a 4° slope. Water moving laterally during overland flow was observed to interact with solutes in the top 2 cm (mixing zone).

It is believed that pesticide extraction from the soil surface into the moving overland flow water is related to diffusion and turbulent transport of dissolved pesticide in soil pores and desorption from soil particles, as well as the dislodgement and suspending of soil particles containing sorbed pesticide (Leonard, 1990). Much of this pesticide extraction is related to

the impact and turbulence created by raindrops. Observations in the field (Buttle, 1990) indicate that high concentrations of pesticides are carried in overland flow, and that the concentration carried reduces with time as the compounds are degraded in the topsoil. At the same time, however, it is interesting to note an increase in soil residues with time in the footslope area compared with up slope as pesticide is carried and then deposited downhill. It was estimated by Buttle (1990) that 0.6-0.9% of the pesticide losses from the field site had been by overland flow. Baker and Laflan (1979) observed greater transport of pesticides in overland flow in plots containing tractor wheel tracks. It was suggested that the wheel tracks by compacting the soil, reduced penetration of surface-applied pesticides into the soil immediately over them. The wheel tracks were also thought to act as a conduit for the surrounding area during heavy rainfall events.

Contamination significance

The importance of overland flow in terms of transporting pesticides directly to field drainage ditches is unlikely to be great as few agricultural fields slope directly into ditches. Translocating pesticides into footslope areas (Buttle, 1990) may have significance in representing a field 'hot spot' from which subsequent vertical bypass flow may transport high concentrations to nearby drainage ditches.

A 2 HYDROCHEMICAL AND BIOLOGICAL PROCESSES

A 2.1 Degradation

The major factor influencing the concentration of pesticide available for transport is degradation. The fate of the vast majority of all herbicides applied to the field is degradation, and depending on the compound and environmental conditions a pesticide may persist for days or months in the top soil. This may result from direct chemical transformation, such as by hydrolysis catalysed by organic matter (Hance, 1987). But almost always soil microorganisms are involved in degrading the compound.

The pesticides may be directly metabolised and the microorganism derive energy from them, presumably because the compounds resemble its natural substrates and so stimulate an appropriate enzyme system to degrade them. An alternative is co-metabolism, in which the microorganism derives no energy benefit. In these situations an enzyme whose production has been stimulated by the presence of another substrate can coincidental catalyse the partial breakdown of the pesticide (Soulas, 1982).

A large number of soil properties can influence biodegradation. Organic matter is of particular importance, as it is often the main factor controlling pesticide adsorption. As degradation of most organic compounds occurs within the bacterial cell, uptake must occur from solution, therefore sorbed species must be desorbed. Where pesticides have a slow desorption kinetics relative to their degradation rate, the degradation rate will be reduced to that of the desorption rate. This was noted with simazine degradation and organic matter content (Walker *et al.*, 1983). It must be noted, however, that microbial activity is often highest in soils with a high organic matter content.

Pesticide adsorption to clay particles has also been observed to reduce degradation rates such as with metamitron (Allen and Walker, 1987) diquat (Weber and Cable, 1968), isoproturon (Blair *et al.*, 1990), and simazine (Walker *et al.*, 1983). Expanding lattice clays have been identified by Sims *et al.* (1992) as having a particular importance in reducing biodegradation.

Another factor to be considered is soil pH, both for its effect on the microbial population and on adsorption where this influences the electronic charge of the compound (Graham-Bryce, 1981). The other main variables that influence degradation are temperature and soil moisture. There is often a 2 to 2.5-fold increase in degradation rate if temperature is increased by 10°C, and a 1.5 to 2-fold increase in rate of loss if soil moisture content is increased by a factor of 2 (Walker, 1991).

The microbial community of the top soil often gives good replication when degradation rates are measured, suggesting a widespread distribution of microbial competence to degrade the compound. Variation in residue concentrations found in the top soil are more likely to be due to errors in spraying than variation in degradation potential (Walker and Brown, 1983). However, the ability to degrade pesticides becomes much more variable with depth (Dictor *et al.*, 1992) leading to generally lower subsurface degradation rates (Pothuluri *et al.*, 1990). A number of suggestions have been put forward to explain this trend, such as lower microbial populations, low nutrient status and a lack of competence to degrade the compound (Pothuluri *et al.*, 1990), all of which may be involved. Little work has been done on the potential for anaerobic degradation of pesticides. This pathway for pesticide degradation may be insignificant in the largely aerobic topsoil, but may be more important in subsurface environments which have low oxygen partial pressures (Pothuluri *et al.*, 1990).

A 2.2 Sorption characteristics

The extent and nature of the sorption and desorption characteristics of a pesticide are influenced by the chemical nature of the compound, and the nature of the surrounding soil particles. Soil particles with a high clay content can present an enormous surface area potentially available for binding such as 100 $m^2 g^{-1}$ (Graham-Bryce, 1981). Broadly speaking, sorption reactions can be divided into hydrophillic and hydrophobic interactions. Hydrophillic reactions are seen as generally more reversible than hydrophobic ones. Hydrophillic interactions with soil surfaces include:

- Hydrogen bonding (sharing a H atom between two electronegative elements).
- Ion exchange (pesticides which act as organic bases will adsorb to cation exchange sites, and those which act as organic acids will adsorb to anion exchange sites, such as alumina or magnetite).
- Covalent or ionic bonds (can occur with reactive groups in organic matter).
- Coordination reactions (ligand exchange, which has been suggested for triazines binding to the transition metals of humic acids)
- Van der Waals forces

Hydrophobic associations or entropy generations can best be described as hydrophobic molecules melting into organic matter. The hydrophobicity of molecules depends on pH, i.e. a pesticide remaining un-charged for example, acting as a weak base would undergo a hydrophobic association reaction with an organic adsorbent in alkaline conditions, but not in neutral or acid conditions. The hydrophobicity of a molecule can be estimated from the octanol/water partition coefficient.

It is worth noting that pesticides can bind to mobile organic fractions such as humic acids. Humics have surfactant properties ie they have hydrophillic and hydrophobic ends and therefore can solubilise hydrophobic pesticides (Graham-Bryce, 1981).

The adsorption potential of a soil is often found to closely correlate with its organic matter content. The organic fraction of the soil is often associated with a high CEC and therefore represents a potential for cation exchange reactions with basic pesticides, and in addition it can undergo hydrophobic associations. The exact nature of all the adsorption interactions that occur with a pesticide in a particular soil are rarely studied, however an apparent change in the adsorption equilibrium with time, leading to greater adsorption, has been noted with certain pesticides (White *et al.*, 1986). This suggests a reduction in the proportion of pesticide immediately available for transport with time. Sorption reactions are time-dependent and rarely take place in situations resembling the typical batch experiments undertaken in the laboratory. Therefore in the disequilibrium conditions of pesticide transport down a macropore for instance, sorption may be much reduced (Kookana *et al.*, 1992) from that which may be estimated in the laboratory. It has also been noted that strongly sorbed pesticides are likely to persist for longer as biodegradation is reduced (Sims *et al.*, 1992; Allen and Walker, 1987).

It would appear that clay soils with a high TOC have the greatest potential for pesticide sorption (Kookana *et al.*, 1992). It must be noted that soils of this type, which retain pesticides in the top few cm, are also maintaining the pesticide in the position where it is most likely to be involved in transport by bypass flow mechanisms.

A 2.3 Volatilization processes

The amount of pesticide available for transport in the water phase can be depleted by volatilization. This process represents a phase change into vapour from the liquid or solid state, which is then followed by vapour dispersion into the atmosphere. The principal features controlling volatilization are (i) vapour pressure of the pesticide (ii) distribution of residues and (iii) the moisture status of the soil.

The vapour pressure of many herbicides used today is very low, such as atrazine, 0.09 mPa (25°C), and isoproturon, 0.0033 mPa (20°C), in which volatilization would be expected to be low. Compounds with a higher vapour pressure such as trifluralin (10.5 mPa at 20°C) have been shown to lose as much as 32% to the atmosphere two days after application (Taylor and Spencer, 1990). In practice the majority of the pesticide is not immediately available for volatilization, being adsorbed to soil surfaces or dissolved in water deep within soil micropores. Therefore, like other pesticide loss mechanisms, volatilization is influenced by soil water content, soil texture and organic matter content. Most rapid losses are likely to occur with residues on the surfaces of bare moist soils (Taylor and Spencer, 1990). Losses from plant surfaces may also be rapid, although residues under the canopy may be in some degree protected by the sheltering action of the leaf cover.

A 3 METHODS OF STUDYING PESTICIDE TRANSPORT

A wide variety of different techniques have been used to study pesticide transport in the past 20 years, from analysis of pesticides in water courses draining catchments of hundreds of hectares to the leachate emanating from re-packed soil columns measuring 10 x 20 cm. Each

method can provide information on pesticide transport and the mechanisms involved. However, the drawbacks and disadvantages of the different methods must be taken into account.

A 3.1 Catchment studies

Pesticide concentrations have been measured in water courses which drain catchments at Swavesy in Cambridgeshire (Harris *et al.*, 1991) and Rosemaund in Herefordshire (Williams *et al.*, 1991). Flow in ditches and streams is measured by v-notch weirs from which a series of water samples is collected automatically, triggered by the flow. Flow, pesticide concentration and rainfall can then be compared. Assessing the relationship between the three is difficult particularly as this is influenced by different pesticide properties. Harris *et al* (1991) reported levels of 1-3 ppb of isoproturon in metered ditches and a maximum level of 13 ppb isoproturon was reported by Williams et al (1991) after a storm event. Williams *et al* (1991) estimated a total of 0.8% of the applied isoproturon escaped from the field to nearby water courses. A difficulty with these studies is partitioning the water balance, such as how much of the rainfall is conducted to the drains as deep percolation is difficult to assess.

Whilst figures generated by these studies are important from the point of view of assessing hazards and modelling, they tell us little about the actual mechanisms involved.

A 3.2 Field plot studies

To get closer to the events that lead to stream contamination it is necessary to work in the field itself. The most methodical approach to studying water movement and pathways within a field has been done at Brimstone on a heavy clay (Denchworth series) soil (Cannell *et al.* (1984). Large 0.3 ha plots have been isolated with polythene down to a depth of 1.3 m and are equipped with trenches, pipes and ditches to study overland flow, lateral interflow and drainflow. However, interpretation is complicated by the difficulty in estimating deep percolation and deep lateral interflow. Isoproturon concentrations in drains from these plots showed up to 50 ppb during rainfall events, and were observed to occur before the formation of a water table in the subsoil. Macropore flow was implicated in the estimated 1% loss of isoproturon from the plots (Harris *et al.*, 1992).

Overland flow has been studied in field sites using isolated, bounded field plots (Buttle, 1990; Baker and Laflan, 1979). These studies have shown the relatively high concentrations of pesticides mobilised during overland flow events (293 ppb metalchlor, Buttle, 1990; 6000 ppb alachlor, Baker and Laflan, 1979) which are found both in solution and adsorbed onto sediment. Because of the variability in microtopography, it is difficult to quantify for a given area how much pesticide is moved in this way; for example wheel tracks left by machinery have a disproportionate influence (Baker and Laflan, 1979).

Suction or porous pot samplers are often used in the field as a way of measuring penetration of pesticides below the soil surface in the soil pore water. They enable estimations to be made of pesticide soil water concentrations below the surface in a non-destructive way (Williamson and Carter, 1991). However, care must be used in the interpretation of results. Suction in the sampling system generates a potential gradient in the suction sampler. The radius of the 'recharge area' may extend to 50 cm or more in all directions. Therefore they may suck water up from groundwater below or via macropores from the soil surface above (Grossmann and Udluft, 1991). As with core sampling mentioned below, low pesticide

concentrations found in the soil pore water at 25 or 50 cm may be misleading; macropores may be conducting high concentrations of pesticides to greater depths, yet remain undetected by these methods.

Many field experiments involve coring or sectioning parts of the field after applications of herbicide and a conservative tracer and irrigation, or rainfall, has taken place. This allows an accurate assessment to be made of the amount and proportion of pesticide/tracer that penetrates into the soil. However, even with a seemingly well defined plot mass balances are often difficult to achieve (Ghodrati and Jury, 1992). The simplest type of experiment involves continuous ponding of water on the soil after application of the pesticide/tracer (Starr and Glotfelty, 1990). However, this seems a rather unrealistic treatment and may induce certain macropores to flow which would not otherwise do so (Trojan and Linden, 1992). Soil coring has shown that under normal rainfall conditions, pesticide concentrations remain at their highest level at the soil surface (often correlated with organic matter) and reduce with depth (Blair *et al.*, 1990). The problems for sampling produced by preferential flow even in sandy soils are well described by Ghodrati and Jury (1990) where the distribution of an acid dye showed some areas with staining down to 90 cm and others less than 40 cm after irrigation.

An alternative approach was provided by Edwards *et al.* (1989), in which wormholes were connected to sampling bottles situated in an underground gallery. On average 29% of the wormholes transported water during rainfall events, but accounted for 1-6% of the rainfall water. Unfortunately not all soils are amenable to digging galleries, although this type of study underlines the potential influence of macropores in pesticide transport.

A 3.3 Lysimeters

An intermediate between the field and the laboratory is provided by the large lysimeter. Crops can be grown and cultivations mimicked, weather regimes can be altered, whilst ^{14}C-labelled pesticides can be used and a mass balance of the compound assessed. The introduction of legislation in Germany which includes lysimeter studies in pesticide registration has increased the number of lysimeter studies now being carried out. Despite being a good representation of the field and a useful research tool, the lysimeter does not completely mimic field conditions. By necessity all lysimeters or undisturbed soil columns are cut off from the parent soil below. This will cause the truncation of macropores, which may then transport water which would not otherwise have happened. In addition, leaching is only considered in the vertical phase and not lateral movement which occurs in sloped fields is ignored. Below 1 m water is lost to the crops as it becomes leachate whereas in the field roots can extend below this depth (Hellpointner *et al.*, 1992). Before water leaches from the bottom of a lysimeter or any soil column the base must first become saturated, a situation which only occurs in the field if a water table is present at the same depth. An alternative is to apply suction to the bottom of the column so that the soil water potential remains the same throughout the profile (Isensee and Sadeghi, 1992). Putz *et al.* (1992) compared the water content of lysimeters with the parent soil from which they have been taken using a neutron probe. The field was found to have a higher water content throughout the year than the parent soil. These drawbacks do not prevent the lysimeter's use as a research tool but they do make the rationale behind its use in pesticide registration more difficult to justify.

A 3.4 Undisturbed soil columns or mini-lysimeters

Smaller undisturbed soil columns provide a more flexible tool for researchers, allowing a wide variety of different treatments or irrigation regimes to be studied, whilst retaining the original soil structure. However, their smaller size can lead to a wide difference between replicates, reflecting the natural inhomogeneity of the soil (Priebe and Blackmer, 1989; Hance and Fuhr, 1992). Their smaller size brings additional problems to that of the larger lysimeter. Whilst soil columns taken from the soil are routinely described as 'undisturbed', researchers are often coy as to the exact details of their extraction from the soil. Often a 10 or 20 cm diameter tube is hammered directly into the soil (albeit at field capacity) prior to extraction. In many soils particularly those with a high clay content, the pressures developed by this process can lead to compaction, additional fractioning and an upward heave of the soil in the centre of the core. A somewhat safer method involves the digging out and exposing of a soil island, enabling the tube to be carefully slid down over the top with minimum force (Cameron *et al.*, 1990). In addition they have all the disadvantages of the larger lysimeter with the so called edge effect being a particularly difficult problem. When water is applied to soil columns/lysimeters the route of least resistance is downward along the wall of the retaining vessel. This is particularly true of soils with a low hydraulic conductivity. Because of the large size of most lysimeters (0.5 - 1.0 m in diameter) this is not so important, but the smaller the diameter of the column, the more important this effect becomes. An effective solution proposed by Cameron *et al.* (1990) is to insulate the soil from the retaining wall with vaseline, applied in the field in liquid form after being heated. Isensee and Sadeghi (1992) used epoxy cement as an alternative method of sealing the soil column.

Notwithstanding these problems, undisturbed soil columns have allowed researchers to get closer to some of the fundamental processes which take place in the field itself. White *et al.* (1986) demonstrated a reduction in leaching volumes with time, as fractures were compressed in a swelling clay soil, whilst Radulovich *et al.* (1992) described two phases of macropore flow using undisturbed soil cores.

A 3.5 Re-packed soil systems

As mentioned above, the natural soil inhomogeneity leads to many problems in interpreting results from soil column work in which a number of different treatments have been used. In an effort to obtain a better understanding of the fundamental mechanisms involved in pesticide transport, particularly with respect to macropore flow, many researchers have used re-packed soil columns in an effort to simplify the system and reduce variables. In these systems the parent soil is sieved and mixed prior to careful re-packing to a bulk density similar to the original soil. To these systems Trojan and Linden (1992) and Ela *et al.*, (1992) added live worms to create natural macropores. A further simplification is to add artificial macropores. With this technique the differences in leaching between a conservative tracer and a pesticide could be observed (Czapar *et al.*, 1992) and related to movement into the matrix with respect to the macropore. Guo *et al.* (1993) and Dao (1991) studied the influence of manure and straw respectively on pesticide leaching in re-packed columns. Ahuja and Lehman (1983) used an imaginative technique of re-packed soil in boxes maintained at a 4% slope, to study the mixing zone associated with overland flow.

A 3.6 Summary of advantages and limitations of different study methods

1. **Catchment studies**

For:	Studying undisturbed natural system Provides important data for modellers and legislators.
Against:	Gives few clues about processes happening in the field.

2. **Field studies**

For:	At the site of the action, can observe the different types of runoff as they occur and study the antecedent conditions which promote them.
Against:	Climate cannot be altered. Wide variability in soil types may occur within the field, leading to different drainage characteristics Installation of equipment may alter field conditions. Mass balance of rainwater or pesticide fate rarely achieved.

3. **Lysimeter studies**

For:	Minimum disturbance to soil physical, chemical and microbiological characteristics. Allow mass balance to be calculated. Climate conditions can be altered and crops grown to simulate different field conditions.
Against:	Water content and drainage conditions may not mimic the field. Expensive and time-consuming. Does not include lateral flow component.

4. **Undisturbed soil columns**

For:	More flexible, easier to control parameters than with large lysimeters. Can study macropore processes in greater detail.
Against:	Drainage can be even less realistic than with large lysimeters, particularly with respect to the edge effect. Variability between replicate soil columns.

5. **Re-packed soil columns**

For:	Researcher has total control over the system.
Against:	Situation created may be totally unrealistic.

Despite more than 20 years of research, many aspects of water movement in soils and solute transport are poorly understood.

For example:
In particular very little data is available on what actually happens in the field in terms of bulk water movement during rainstorms and the amounts of pesticide associated with the different flow pathways.

Whilst macropores have often been highlighted to be of key importance in pesticide contamination of surface water courses and groundwater, many aspects of their function are not yet fully understood, for example:

- How pesticide is released from soil particles during rainfall events, is it removed

from the solid phase, and how is this influenced by rainfall intensity?

- The movement of water through a topsoil mixing zone prior to entry into a macropore.
- The difference in behaviour between the different types of macropore.
- The interaction of water and solutes with the surrounding soil matrix
- The relationship between neighbouring continuous and discontinuous macropores.

Against this background each of the different methods described above have something to offer the researcher provided their drawbacks and limitations are appreciated.

A 4 ISOPROTURON LOSSES FROM AGRICULTURAL LAND

Williams *et al.* (1991) and Harris *et al.* (1991) have measured isoproturon in streams draining defined catchments from clayey soils. At Rosemaund (Bromyard series) a peak concentration of 13 ppb was detected in an instrumented stream following a rainstorm event. It was estimated that 0.8% of the applied isoproturon escaped from the field into the surrounding water courses (Williams *et al.*, 1991). At Swavesy (Denchworth series) Harris *et al.* (1991) detected levels of 1-3 ppb in ditches draining the catchment. Levels of 0.25 to 0.75 ppb isoproturon were detected in the river Granta from January to May draining a Chalk catchment (Clark and Gomme, 1992).

Levels of 10-50 ppb isoproturon have been detected in the drainage from the 0.2 ha mole field plots at Brimstone after a 2.5 kg/ha application in winter seasons (Harris, 1991; Harris *et al.*, 1992). Up to 100 ppb isoproturon concentrations have been detected in lateral interflow in similar experiments (Harris *et al.*, 1993). In contrast to winter applications, concentrations as high as 550 ppb have been detected in drainwater after spring applications (Harris *et al.*, 1993) although in smaller volumes of water. Total reported losses of isoproturon to drainwater over drainage seasons at Brimstone have been assessed as $< 1\%$. It would appear that throughout most of the drainage seasons the water table was below the depth of the mole drains. Therefore water must have entered them from above via cracks, with hydrographs showing peaky responses to rainfall. The peak and total water involved in drainflow was related primarily to the soil moisture status. A reduction in drainflow peaks in response to rainfall was noted over a number of years as the mole drains deteriorated (Harris, 1991).

Degradation experiments under simulated field conditions give isoproturon a DT_{50} of 30 days (Blair *et al.*, 1990) and a greater persistence in soils with a high clay content has been noted. Mudd *et al.* (1983) reported a DT_{50} of 40 days in field experiments with a sandy loam soil but noted that a small remaining proportion of isoproturon ($< 4\%$) persisted beyond 203 days. This suggested that a proportion of isoproturon was protected in some way from degradation, possibly due to irreversible adsorption to an organic fraction. In addition Harris (1991) noted isoproturon in drain water (at a low concentration) emanating from plots which had not had a pesticide application, so the pesticide may have been a legacy of a previous year's application.

Annex B Staff list

A large number of IH staff have contributed significantly to this project, these include:

Project Supervision:	Dr P. Whitehead, Dr C. Batchelor
Project Coordination:	Dr A. Johnson
Soil Hydrology:	J. Bell, A. Haria, D. Robinson,
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Hydrology and Modelling:	R. Williams, C. Volkner, A. O'Donohue
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Instrumentation:	M. Turner, Dr T. Dean
Worshops:	A. Warwick, G. Walley, J. White
Transport and Site Services:	J. Fraser, I. Standbridge, R. Drewett

Annex C Glossary of terms

Suction samplers	Also known as suction cups or suction candles. Consist of plastic tube with ceramic bulb at the end. Installed in the soil at different depths and water extracted by applying suction.
Overland flow	Also known as surface runoff. Term used to describe water moving over the soil surface, both for limited distances (a few cm) and during sheet flow, when water may transport solutes over many tens or hundreds of metres.
Lateral interflow	Term used to describe lateral movement down the slope within the soil, ie below the surface.

Appendix 2 Total impact assessment of pollution in River Basins: Pesticide Impact Modelling

Draft Final Report R&D Project 119

Total Impact Assessment of Pollution in River Basins: Pesticide Impact Modelling

Institute of Hydrology

December 1993
R&D 119/9/W

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EXECUTIVE SUMMARY

This document describes the research on the movement of pesticides to surface waters carried out at ADAS Rosemaund over the period 1987 to 1993. The work was jointly funded from the NRA R&D programme and the Institute of Hydrology Science Budget. The project involved close collaboration with the following organizations; Ministry of Agriculture Fisheries and Food, the Building Research Establishment, the University of Birmingham, the Soil Survey and Land Research Centre, ADAS Soil Water Research Centre and ADAS Rosemaund.

NRA proposals for Water Quality Objectives will probably include pesticide standards which already exist for the protection of aquatic life, and for surface waters used for potable water abstraction. Pesticide limits may also be included in other use related objectives and EC Directives, yet to be defined. It is vital therefore that the movement and fate of pesticides in the aquatic environment is well understood and predictable so that the NRA can seek to control diffuse inputs of such chemicals and ensure compliance with the statutory objectives. Without such information it is difficult to envisage how compliance with such standards could be achieved. This study has sought to increase understanding of pesticide run-off and to provide tools for its prediction.

The concentrations of pesticides have been measured at two points in the stream draining the Rosemaund catchment and from two sub-surface drainage systems. The measurements were taken principally during rainfall events that occurred after the application of a number of pesticides selected to cover a range of generic types and physico-chemical properties. Occasional samples were taken before and between events to assess background levels. Details of sampling methodology are reported.

This sampling programme has established that the use of pesticides, even when applied according to normal agricultural practice, will probably lead to the contamination of surface waters in the catchments into which they drain. Of the 93 event/pesticide/site combinations monitored, maximum concentrations were distributed as follows; 9 below detection limit, 17 between detection limit and 1 µg/l, 40 between 1 and 10 µg/l and 25 above 10 µg/l. The magnitude of pesticide runoff events is discussed in terms of pesticide physico-chemical properties. The pattern of pesticide runoff through individual events is characterized and discussed.

A model for estimating pesticide runoff at Rosemaund is presented and tested against data collected during the study. The model performed well in estimating the peak concentration although the timing of the peak was usually in advance of that observed. The limitations and assumptions of the model are listed. An example of how the model might be used to help in setting a sampling strategy for Rosemaund is given.

The extension of modelling to larger catchments is discussed and a possible approach outlined. The use of such models in setting environmental quality standards for pesticides as non-point source pollutants is discussed. This application is extended to consider the establishment of sampling strategies.

The importance of the study to the NRA is highlighted and some strategic recommendations made.

KEYWORDS

Pesticides, modelling, runoff, non-point source pollution, sampling strategies, Environmental quality standards.

1. INTRODUCTION

The use of pesticides in agriculture has risen dramatically in recent years. This has been due mainly to the introduction of effective annual grass weed herbicides in the early 1970's which allowed the continuous growing of autumn-sown crops on heavier soils, and effective cereal fungicides in the mid-1970's. This increase in pesticide usage has led to serious concern about possible contamination of the environment by these chemicals. One important environmental medium at risk from contamination with pesticides is the aquatic environment, and the effect of pesticides, both directly on aquatic life and indirectly on potable water supplies are of particular concern.

Reviews of pesticides in drinking water sources in England and Wales (Lees and McVeigh, 1988; Drinking Water Inspectorate, 1992) have indicated that a number of sources may contain individual pesticide levels greater than the Maximum Acceptable Concentrations (MAC) laid down in the European Community Drinking Water Directive (Council of the European Communities Directive, 1980). This directive stipulates a MAC of any single pesticide in potable waters of 0.1 µg/l and a MAC of 0.5 µg/l for total pesticides. Although these MACs may be over-cautious from the standpoint of human health, the failure of a proportion of samples to comply has caused public concern. As the range and complexity of pesticides in use increases the risks of breaching MAC values in drinking water and the difficulties of detecting and controlling diffuse inputs of pesticides also increase.

The Water Act 1989 (and subsequently the Water Resources Act 1991) allows for the Secretary of State to derive a classification system for controlled waters and to set Water Quality Objectives (WQOs) for those waters. The Department of the Environment has indicated its intention to introduce WQOs and the consultation process has begun. The NRA will be responsible for ensuring compliance with these statutory WQOs and has published consultation proposals for WQOs which include: a new general classification scheme for controlled waters, use related objectives and standards and incorporation of the requirements of relevant EC Directives.

Some pesticide standards already exist for the protection of aquatic life, and for surface waters used for potable water abstraction and, if the NRA proposals are implemented, they may be incorporated in to the WQOs for appropriate rivers. HOwever, pesticide limits may also be included in other use related objectives and EC Directives, yet to be defined. It is vital therefore that the movement and fate of pesticides in the aquatic environment is well understood and predictable so that the NRA can seek to control diffuse inputs of such chemicals and ensure compliance with the statutory objectives. Without such information it is difficult to envisage how compliance with such standards could be achieved.

Published data on pesticide concentrations in field drains and streams are available, but such studies generally originate from North America, where agricultural systems are often irrigation-based rather than rain-fed as in the UK (Johnston *et al.*, 1967; Frank *et al.*, 1982; Spencer *et al.*, 1985; Muir and Grift, 1987; Thomas and Nicholson, 1989; Wauchope, 1978). In addition to this, in most cases details of agrochemicals used in the respective catchments can only be estimated (Hennings and Morgan, 1987; Gomme *et al.*, 1992), and consequently the value of these studies is limited. There is therefore a need to study agrochemical mobility under experimental conditions in controlled catchments in the UK.

In addition to the need for field data on pesticide concentrations in the aquatic environment, there is also a requirement for accurate predictions of run-off patterns of currently used products from particular watersheds on the basis of land use and agricultural practice. Such descriptions or models would be invaluable to the agencies responsible for aquatic environmental regulation and control in the UK, i.e. the National Rivers Authority (NRA) in England and Wales and the River Purification Boards in Scotland.

It was for these reasons that a review of the agrochemical pollution problem was undertaken by the Institute of Hydrology (IH) in 1985-86 funded by the Department of the Environment (DoE). As a result of the review the DoE funded a catchment study of pesticide runoff by IH and the Welsh Water Authority (subsequently the Welsh Region of the NRA) based at and supported by personnel of the ADAS Experimental Husbandry Farm at Rosemaund near Hereford. When the study started in autumn 1987, IH was joined by the MAFF Fisheries Laboratory, Burnham on Crouch in collaboration with the Building Research Establishment (BRE) who had a mutual interest in pesticide transport. A more detailed description of the history of the project and the way in which collaboration was organized is given in Section 2.

The ADAS Rosemaund Farm site was chosen principally because the stream catchment is contained almost entirely within its boundaries. This allows good knowledge of pesticide applications to the entire catchment, essential if the data produced are to be used for the development and calibration of models. Further, the use of an experimental farm allows some influence over the selection of pesticide groups to be studied, provided that they are applied within the constraints of Good Agricultural Practice. Finally, the geology and soil structure prevent significant loss of rainfall to ground water, thus maximising chemical transport to the drains and the outflowing stream.

1.1 Objectives

The overall project objective was to investigate the pollution by pesticides of streams draining agricultural catchments and to develop a model of the movement of pesticides from the point of application to receiving streams. Within this overall objective there were a number of specific objectives:

1. To assess the movement and distribution of selected pesticides in surface waters.
2. To develop a simple flow and concentration model of the movement of pesticides from the point of application in a catchment to the receiving stream.
3. To develop management recommendations for pesticide usage strategies, drawing together the full study findings , including those of collaborative bodies.
4. To derive guidance for appropriate sampling strategies for pesticides in watercourses.

2. BACKGROUND

The path that led to what is now known as the Rosemaund Pesticide Runoff Study is somewhat complicated. It is, therefore, useful to review the history of the project with respect to the various sources of funding that have been brought to bear and the formalization of the scientific collaboration through the Management Steering Group.

The establishment of a catchment study of the movement of pesticides to surface water arose as a result of a literature review entitled 'Total Impact Assessment of Pollutants in River Basins: A feasibility Study', carried out by the Institute of Hydrology (IH) on behalf of the Department of the Environment (DoE) in 1985/86 (Whitehead *et al*, 1986). The study covered a review of integrated catchment hydrology and water quality models and agrochemicals, their use and chemistry. Among the conclusions of the study was the need for detailed information on agrochemical inputs and outputs on the catchment scale that could be used for the development and testing of mathematical models. It was therefore proposed that catchment studies would be set up in conjunction with the then Water Authorities in order that this data might be produced. Of the Water Authorities approached only the Welsh Water Authority (WWA) and the Wessex Water Authority (WeWA) were prepared to support such a study. Although catchments were set up with both these Authorities only the collaboration with Welsh Water Authority proved fruitful. The instrumentation of the Rosemaund catchment was thus started in 1986/87 in time for the autumn applications in 1987.

At about this time the Ministry of Agriculture Fisheries and Food (MAFF), Fisheries Laboratory at Burnham-on-Crouch together with the Building Research Establishment (BRE) were interested in the possibility of using mathematical models as part of the registration process for new chemicals. They were interested in the use of a simple fugacity model (Mackay and Paterson, 1981; Brooke and Mattheissen, 1991), and needed data on pesticide transport in order that the model could be tested and hopefully validated. MAFF Burnham were considering generating their own data for this exercise and it was decided that it would make good sense for them to conduct their field work at the same site as IH/WWA. Thus MAFF Burnham and BRE set up their experiments in the headwaters of the Rosemaund catchment (see Section 3.2).

After the second season of observations it became clear that more information on the in field processes was required if any real understanding of pesticide movement was to be made. One of the fields above the MAFF monitoring site was chosen for detailed study. MAFF sub-contracted the Soil Survey and Land Research Centre (SSLRC) to deploy soil water suction samplers and to carry out a detailed soil survey. IH funded its own Agrohydrology section to install equipment to study the movement of water through the soil profile to the tile drains. At about this time both the MAFF and IH had cause to call on the expertise of the ADAS Field Drainage Experimental Unit (FDEU) to establish structures, initially for the measurement of drainflow and subsequently to revamp the weirs in the stream. More details of the sampling strategy and the methods employed are given in Section 3.2.

In order to coordinate the activities of all the groups working at Rosemaund a management structure was introduced. To direct the scientific strategy behind the research a management steering group was set up, chaired by the Director of ADAS Rosemaund and with representatives from each of the main funding bodies, IH, WWA (later the National Rivers

Authority (NRA)) and MAFF. The integrated running of experiments was achieved through a Technical Group made up from one or more representatives from each of the collaborating organizations.

During the course of the study the funding of the Institute of Hydrology passed from the DoE to the NRA on its formation in April 1990. The role of WWA being taken over by the Welsh Region of the NRA. Inevitably the splitting up of the Water Authorities into the NRA and creation of the NRA and private water utility companies caused some problems. These were especially noticeable in the chemical analysis which had to be transferred from the WWA laboratory at Bridgend to the NRA laboratory in Llanelli. More details of the arrangements for chemical analysis are given in Section 3.5.

The collaboration of the groups working at Rosemaund has added greatly to the research of the individual groups. While individual establishments have had their own objectives and contractual obligations, a joint set of objectives was established in order to give a clear direction to the collaboration. These were:

1) To asses the movement, distribution and environmental impact of selected pesticides in surface waters.

2) To investigate, develop and validate hydrodynamic models of the movement and fate of agricultural pesticides between the place of application and the receiving watercourses, on a whole catchment basis.

3. METHODS

3.1 Study Site

The study catchment lies mainly within the boundaries of ADAS Rosemaund 15 km north east of Hereford, UK (Fig. 3.1). The farm is owned by the Ministry of Agriculture Fisheries and Food (MAFF), operated by ADAS and has been managed as an experimental unit since 1949. The catchment has an area of 1.5 km^2 with an altitude range of 76 m to 115 m and correspondingly gentle slopes. The soils are from three series, the Bromyard, the Middleton and the Compton and have been mapped and analyzed by the Soil Survey and Land Research Centre (SSLRC), (Fig 3.2). The Bromyard series comprises two phases, the normal and the shallow phase, differentiated by the depth to the underlying geology. The Bromyard series predominates and is found on the slope areas of the catchment. The wetter Middleton and Compton series tend to occur on flatter ground and towards the lower end of the slopes. Details of the soil textures of the four main series are given in Table 3.1. Generally the soil texture is silt clay loam in the top 60 cm changing to silt loams below this depth, the largest clay fraction being between 25 and 60 cm below the surface. The soil is subject to considerable cracking following periods of low rainfall during the summer months. The organic matter content of the surface 25 cm cultivated layer under long term arable cropping is within the range of 1 - 3 per cent with little organic matter present below 35 cm. The geology is made up of effectively impermeable siltstones and mudstones from the devonian era which lie between 1 m and 3 m below the surface.

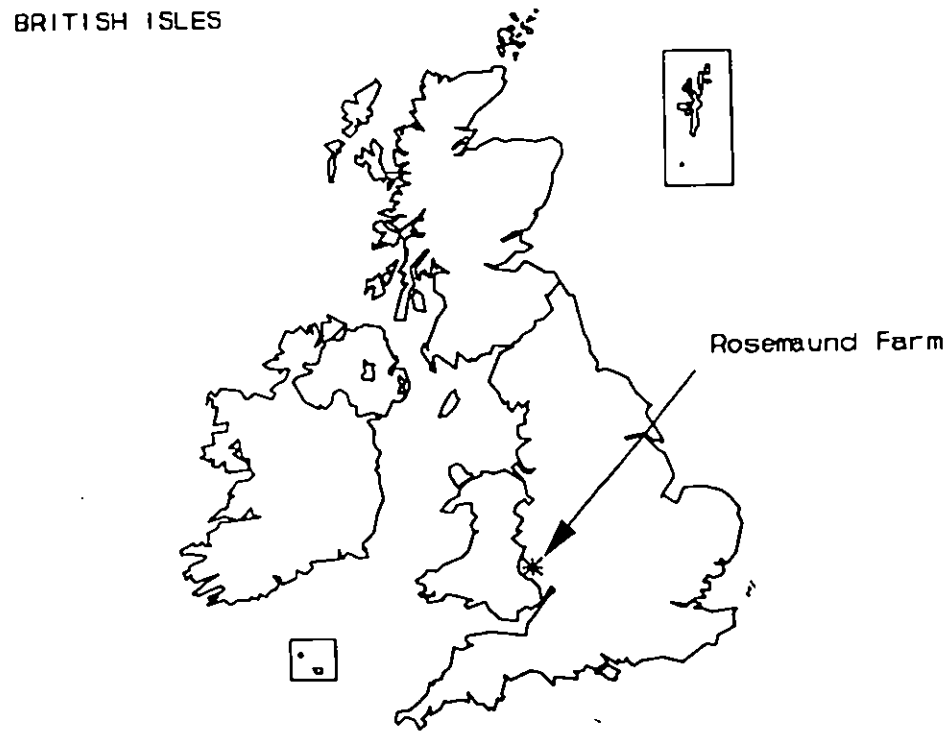

Figure 3.1 Location of the Rosemaund Catchment within the British Isles.

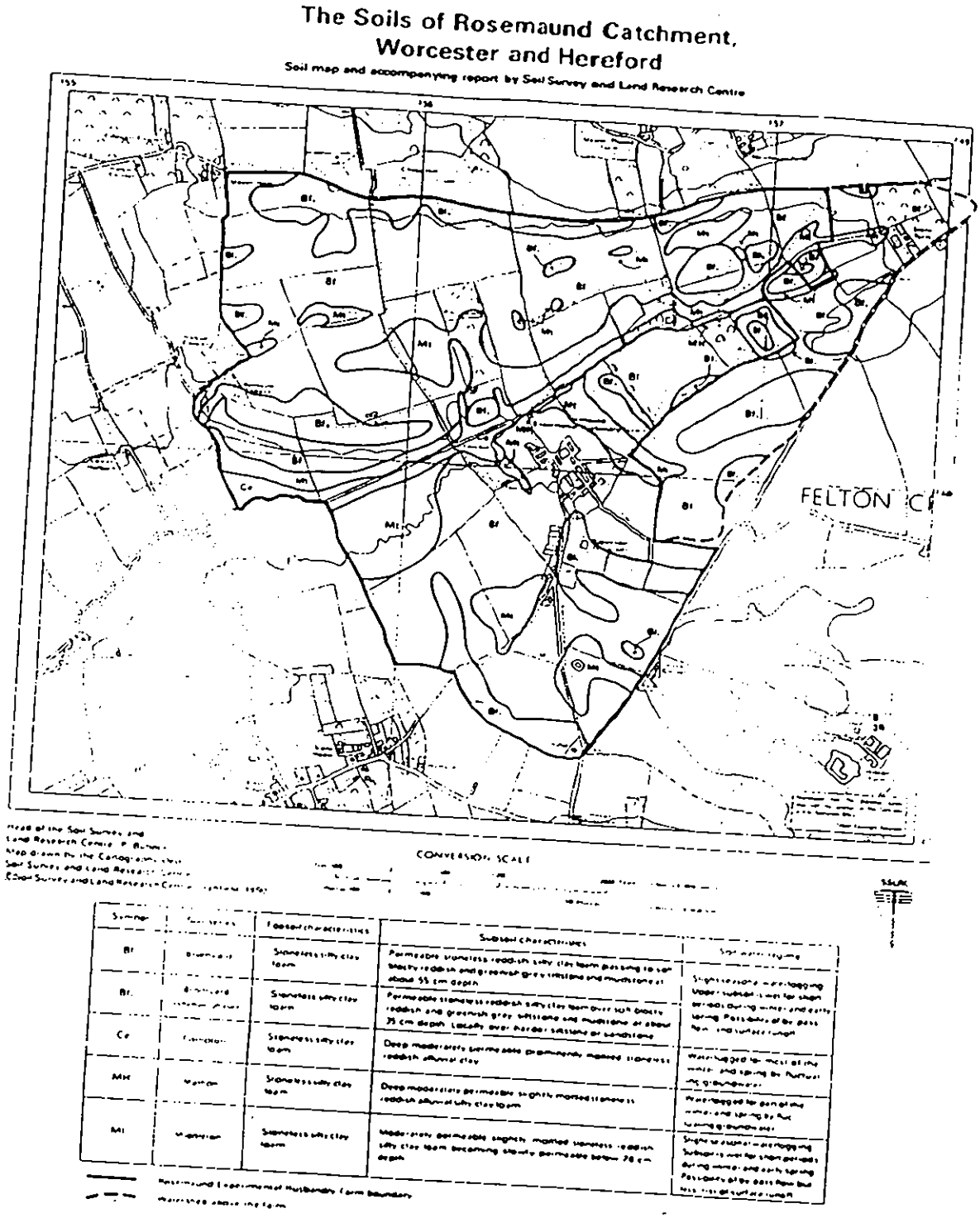

Figure 3.2 Map showing the distribution of the main soil series at ADAS Rosemaund.

Table 3.1 **Physical properties of the soil profiles for the soil series found at ADAS Rosemaund.**

Soil Series	Depth (cm)	Sand (%)	Silt (%)	Clay (%)	Organic Carbon (%)	pH (1:2.5) in water
Bromyard (Normal Phase)	0-30	9.0	60.0	31.0	1.66	6.3
	30-48	10.0	58.0	32.0	0.91	6.8
	48-67	5.0	52.0	43.0	0.66	6.7
	67-83	4.0	50.0	46.0	0.37	6.7
Bromyard (Shallow Phase)	0-22	1.0	70.0	28.0	1.80	6.3
	22-31	3.0	66.0	30.0	1.35	6.5
	31-60	3.0	71.0	28.0	0.30	6.2
	60-78	1.0	73.0	26.0	0.28	5.8
	78-112	1.0	79.0	20.0	0.29	5.8
Middleton	0-32	3.0	49.0	48.0	2.84	6.6
	32-40	0.0	51.0	49.0	1.56	7.0
	40-55	0.0	52.0	48.0	1.11	7.3
	55-74	0.0	68.0	32.0	0.62	7.2
	74-112	2.0	60.0	38.0	0.48	7.1
Compton	0-22	3.0	46.0	51.0	3.30	6.7
	22-30	2.0	45.0	53.0	2.34	6.9
	30-65	2.0	56.0	42.0	0.57	6.9
	65-80	0.0	47.0	53.0	0.88	7.1
	85-105	4.0	49.0	47.0	5.51	6.5
	105-115	5.0	52.0	43.0	7.63	6.3

The land within Rosemaund Farm is used for a wide mixture of agricultural enterprises. Of the 176 ha, approximately 30 % of the area is grassland, another 40 % of the farm is in cereals with 20% in oilseed rape, peas and root crops and, 10 % is in hops. The average annual catchment rainfall is 664 mm. The catchment is drained by a single stream that continues to flow (mean flow 11 l/s) in all but the driest years. The stream flows into the River Lugg which is a major tributary of the River Wye. Most of the fields have been under drained using plastic pipes at a depth of 1 m, with permeable backfill to within 500 mm of the surface. The average drain spacing is 20 m (Fig 3.3).

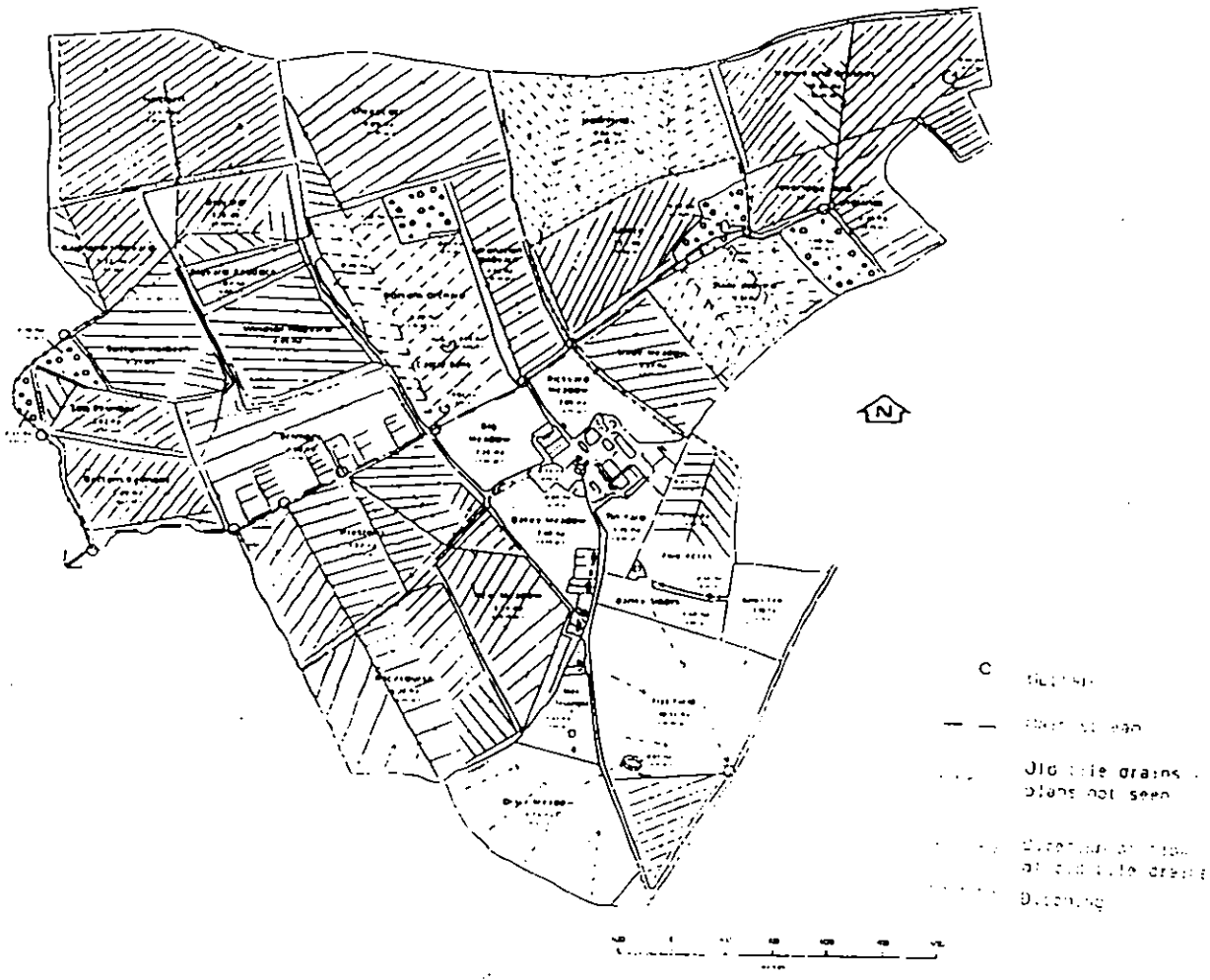

Figure 3.3 **Map showing the extent of the sub-surface drainage system at ADAS Rosemaund.**

3.2 Sampling Strategy

The original objective of the study was to monitor the pesticide runoff from an agricultural catchment under conditions of normal agricultural practice. A monitoring site was chosen close to the point where the stream left the land farmed by ADAS Rosemaund in order that as much of the agricultural activity as possible was included. (site 0, Fig. 3.4). The monitoring strategy adopted was designed to measure pesticide concentrations in the stream resulting from rainfall events falling on recently treated fields within the catchment. Thus an automatic sampler was used to take a series of water samples at short intervals (usually one hour but intervals of half and four hours were also used) over the duration of rainfall events. In order that these concentrations could be linked to the hydrological response of the catchment a flow measuring structure was built in the stream at the monitoring site. Stream samples were also

taken manually every two weeks to assess the baseflow concentrations before and after rainfall events. At around the same time MAFF established a similar monitoring site and sampling protocol farther upstream (site 1, Fig. 3.4).

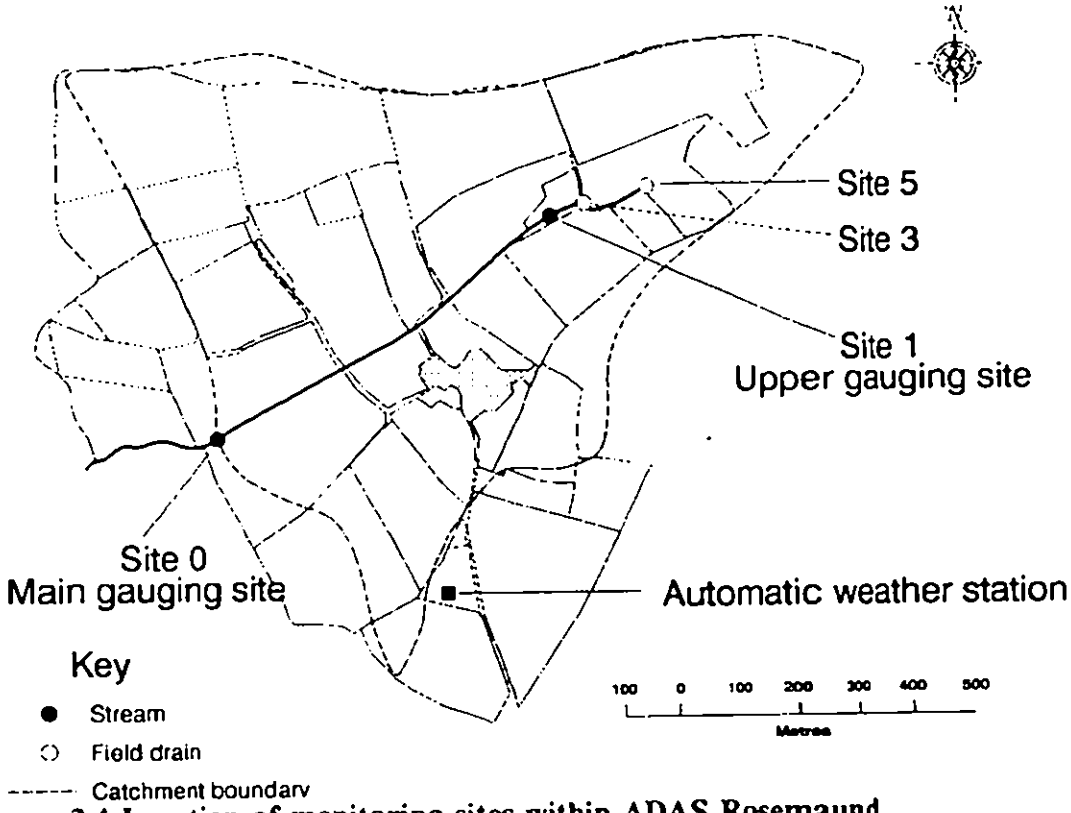

Figure 3.4 Location of monitoring sites within ADAS Rosemaund

Later in the study, as the emphasis shifted more to understanding the processes that control pesticide movement, additional monitoring sites were established. The new sampling sites were chosen to represent the tile drainage system that existed in the majority of the fields at ADAS Rosemaund. Thus IH started to monitor the drain leaving the field known as Longlands (site 5, Fig. 3.4) and MAFF started to measure pesticide concentrations in the outfall from the drainage system under part of the fields known as Foxbridge and Stoney and Brushes, (site 3, Fig. 3.4).

Additionally, SSLRC soil suction samplers were deployed within Longlands field in order to estimate the pesticide concentration in solution at different depths through the profile. Throughout the study soil samples were taken, by BRE, from Foxbridge and Longlands and Stoney and Brushes following selected applications so that total soil residues could be monitored.

In the final phase of the study, an investigation of the particulate movement of pesticides was undertaken for highly-sorbed chemicals. Four surface runoff traps were located in Longlands field to monitor surface movement of pesticide during rainfall events. Additionally, sediment

traps were placed in the stream bed at site 1 and site 0, to measure the concentration of pesticide in bed sediments mobilized during rainfall.

To summarize, within the catchment four monitoring sites were instrumented. At each site flowrate was measured continuously while chemical samples were taken at frequent intervals during rainfall events following pesticide application and less frequently between events. Total soil residues were monitored following application as was the soil water pesticide concentration at different depths.

Although IH was responsible for only part of the sampling carried out at Rosemaund, details of the whole catchment monitoring programme are given here for completeness. The precise methods used to carry out the programme are given in Sections 3.2.1 to 3.2.3.

3.2.1 Stream Flow Measurement and Meteorological Data

Stream flow was calculated from the stream level retained behind standard V-notch and rectangular notch weirs as appropriate. The stream level being recorded at 15 or 30 minute intervals (Matthiessen *et al*, 1992).

The primary source of meteorological information used in the study was an IH Automatic Weather Station (AWS), (Strangeways, 1972, 1976). This instrument takes readings every 5 minutes and averages or sums them to provide hourly values of the following variables:

- Rainfall
- Wet and dry bulb temperature
- Solar and net radiation
- Wind speed and direction
- Soil temperature

ADAS Rosemaund staff maintain a full daily Meteorological Office weather station and this provided a backup system for the AWS. The AWS was located within the Meteorological Station site (Fig. 3.4).

3.2.3 Pesticide Sampling

Water Samples

Water samples were taken from sites 0,1,3 and 5 as indicated in figure 3.4. At all locations, water samples were taken during rainfall events and background samples were taken for a limited time before and after the rainfall events. The method of sampling was similar at all sites. Rainfall event samples were collected using two types of automatic water samplers, a suction sampler and a peristaltic pump sampler. Both samplers collected samples into 24 one-litre brown glass bottles. To minimise the risk of contamination and/or loss of active ingredient, the sample tubes were made from PTFE and the internal parts of the samplers were almost entirely constructed from stainless steel or coated with PTFE. Up until June 1988 the samplers were started when a predetermined amount of rain had fallen in a given time.

After that date a method which started the sampler when the stream rose to a specified level was employed. The latter has proved more reliable.

Soil Samples

Soil samples were taken from the fields onto which the herbicides had been applied. They were taken from randomly chosen points on the intersects of a 25 m grid superimposed on the fields. Samples were taken to a depth of 1 m using a steel corer. Cores were placed in plastic bags, sealed, and then stored at -20 degrees C until analyzed. The frequency of the sampling was based on the expected lifetimes of the chemicals in the soil. In addition, samples were taken as soon as possible following a rainfall event. In all cases samples were taken to give a mean soil pesticide concentration in the top 1 m of the soil.

Soil Water Samples

Soil water samples were collected by SSLRC using soil suction samplers constructed of inert material designed specifically for pesticide studies. The design of the samplers is shown in figure 3.5. Samplers were installed at 50, 100 and 150 cm depths at various locations in Longlands (Fig 3.7) throughout the 89/90, 90/91 and 91/92 seasons. Each sampling location had a number of replicate samplers. Each sampler was installed in the following manner. A 10 cm diameter hole was augured to just below the require monitoring depth and the bottom lined with dry sand. The sampler was placed on the centre of the sand with the mid-point of the cup at the require depth. Further sand was poured in to pack around and cover the ceramic cup. Sand is used to ensure good hydraulic contact and also as a reservoir for percolating water. Excavated soil was firmly repacked horizon by horizon and the most clayey horizon compacted in the hole to prevent preferential vertical water movement to the ceramic cup. In the later two seasons Bentonite clay was also used as an extra guarantee.

The sampling strategy for the suction samplers was to respond to all events of 10 mm or greater falling after application of the target pesticide. A vacuum of 700 mbar was applied to each sampler using a hand held pump. The suction was left over night and the water drawn to the sampler was recovered the following day and transferred to amber glass bottles. Any residual suction in the samplers was noted on collection of the sample.

Surface Runoff Samples

Surface runoff samples were collected using SSLRC surface runoff traps (Fig 3.6). The traps were 1 m wide steel troughs with 3 short pipes protruding from one side, while the other side was sloped with a 10 cm wide lip. The sampler was placed into a hole in the soil with the sloping side was placed facing up-slope and the lip inserted into the soil at a depth of about 1 cm. A lid was placed over the trough to stop direct capture of rainwater. Brown glass bottles were placed on the ends of the pipes to collect the water trapped by the sampler. After a rainfall event the bottles were collected and replaced with new bottles. The contents of the three bottles were combined before being analyzed for the target pesticide.

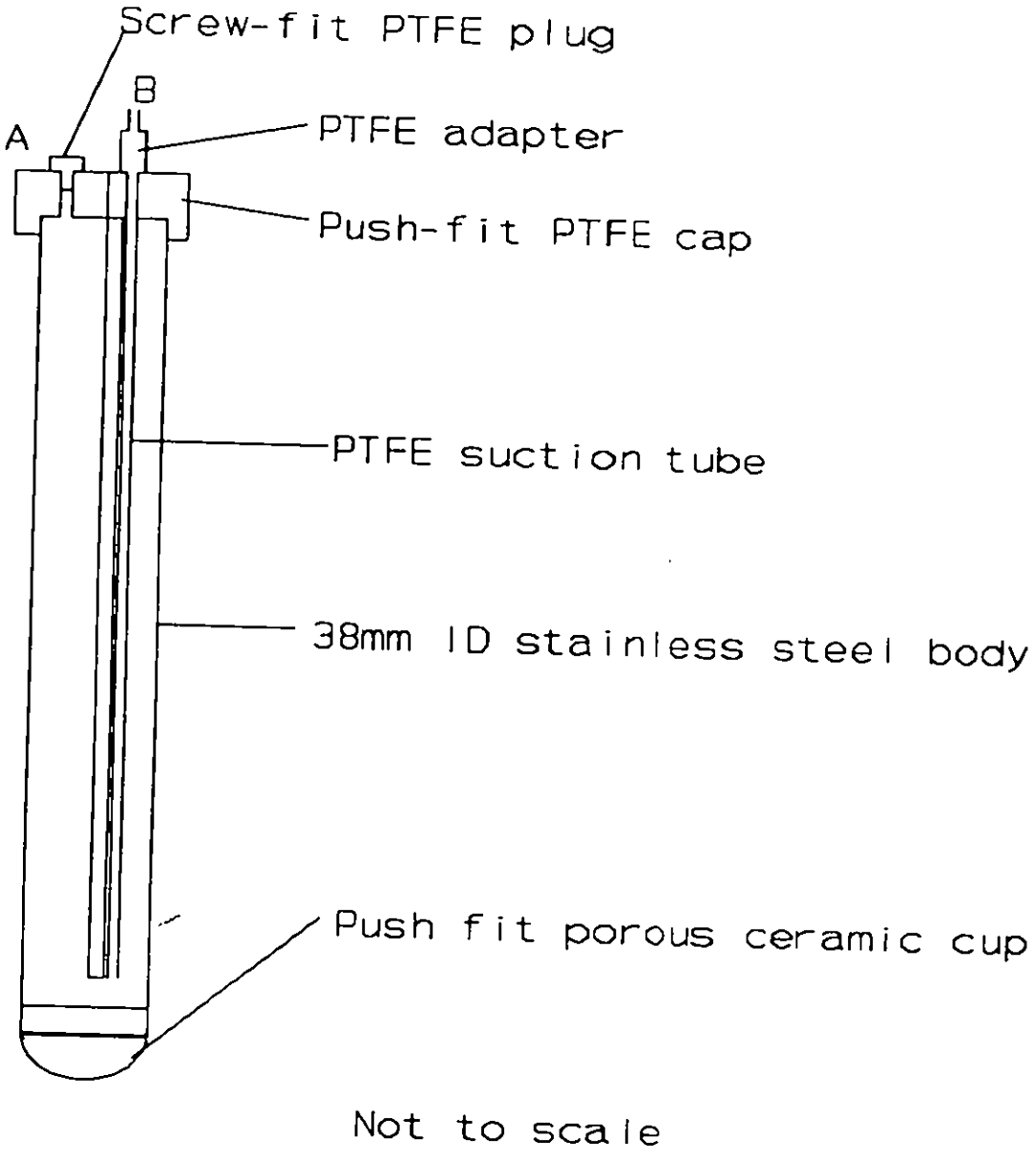

Figure 3.5 **Detail of an SSLRC soil suction sampler used for sampling extracting soil water samples.**

Bed Sediment Samples

The sediment sampler buckets (manufactured from PTFE coated stainless steel) were located in pits dug in the stream bed. These were of such a depth that approximately 2.5 centimetres of the bucket wall protruded above the stream bed. This method was used to trap only the mobile bed sediments that settled out during or after events.

After each rainfall event the buckets were removed carefully from the stream-bed with as little disturbance as possible to the collected sediment and moved to a safe site. A new clean bucket was used to replace the old bucket in the pit, again, ensuring the minimum disturbance

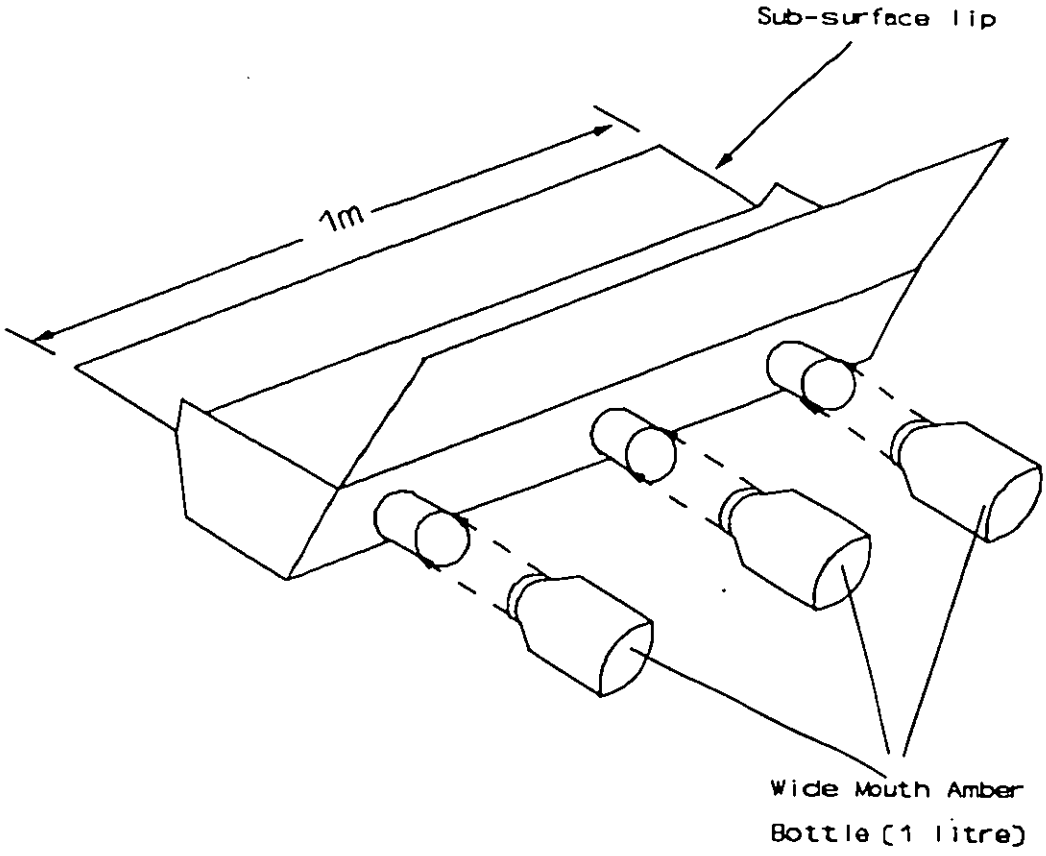

Figure 3.6 Detail of a surface runoff interception trap.

to the site. If, in the moving of the bucket, there was disturbance of the collected sediment, the sediment was allowed to settle before further processing. With the sediment stable and settled, surplus water was decanted off until the sediment itself started to be disturbed. The sediment was then poured into the sample bottles. These bottles were 0.5 l wide mouthed jars. Any remaining sediment was 'swept' into the bottle, using a PTFE spatula. The bottles were sealed and labelled.

3.2.4 Soil Hydrology

The soil hydrology experiments at Rosemaund started in the Autumn of 1989 and continued for three crop years ending in the summer of 1992. The objective of this part of the study was to gain an insight into the soil water pathways through and over the soil profile and how these might influence pesticide movement. Once determined, these pathways would become the foundation for a physically based model of pesticide movement within the Rosemaund catchment.

The soil-physics experiments were carried out in Longlands field. Figure 3.7 shows the location of the experiments over the duration of the study. Although the detail of the experimental design was modified and refined throughout the 3 years of the study, basic philosophy remained the same. Arrays of mercury manometer tensiometers were used to

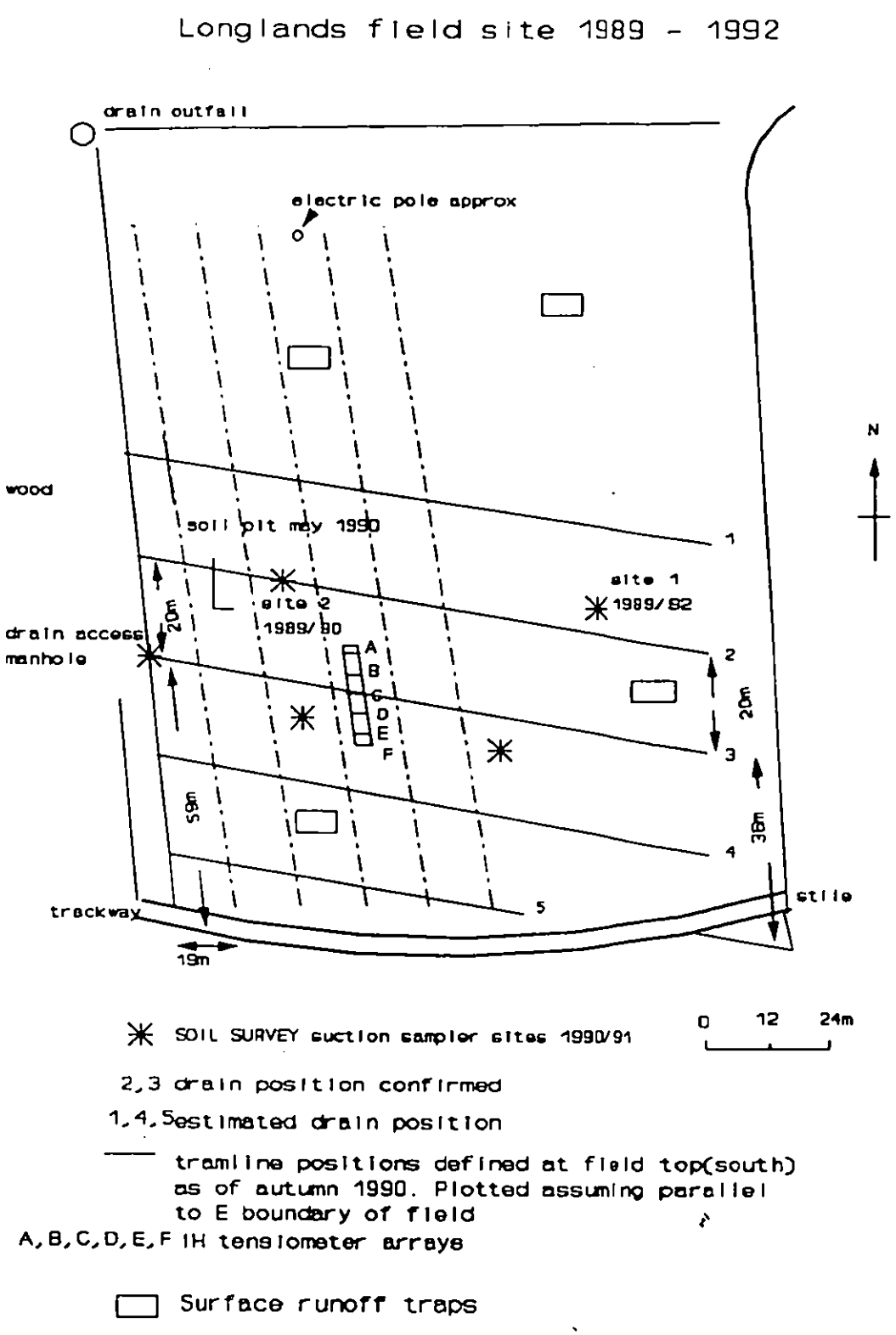

Figure 3.7 **Layout of instrumentation in Longlands field over the duration of the study. The exact location of some equipment will have changed from year to year.**

determine the soil water potentials both down the soil profile and across the slope of the field. Soil water contents were also measured using a neutron probe. In the light of the importance of the tile drainage system on water movement, the final experimental design concentrated on the soil water potentials around a representative drainage element. Figure 3.8 shows the layout of tensiometers used in the 1990/91 crop season. Soil water potentials were monitored within a vertical plane extending 10 m on either side of the line of a field drain to the mid-drain position. An array of tensiometers was set out as six profiles, each of six tensiometers, at depths 10, 30, 60, 90, 120, and 150 cm.

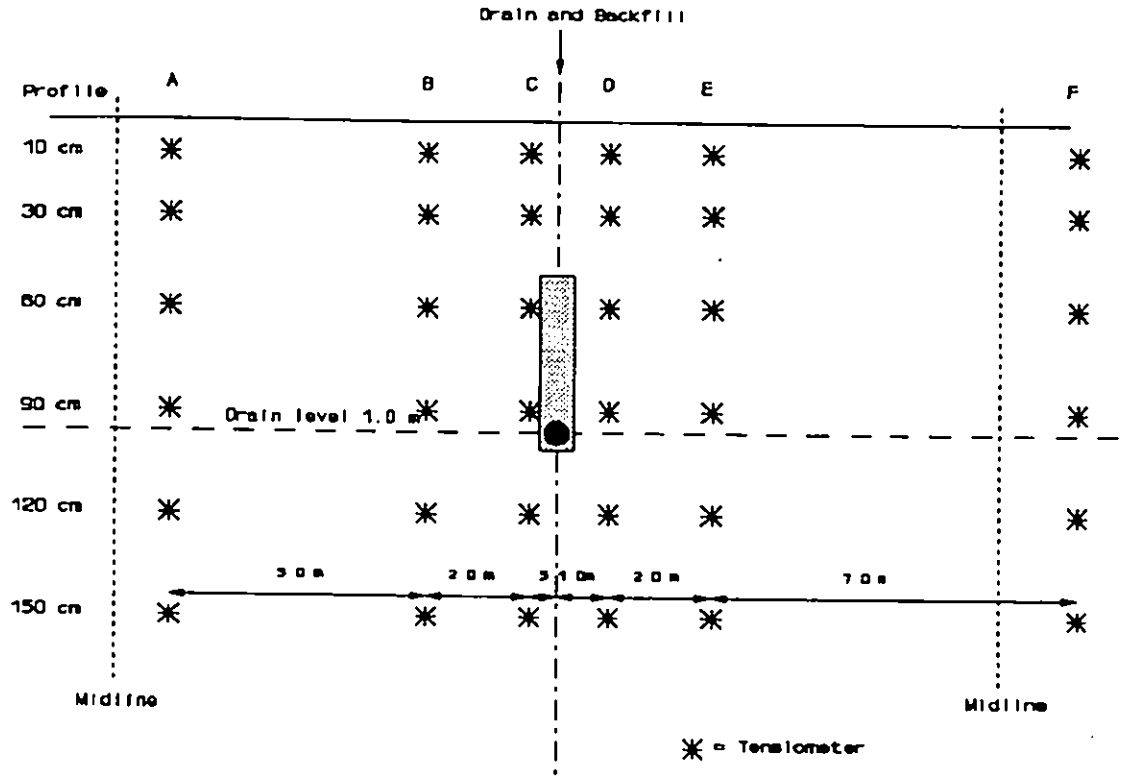

Figure 3.8 Diagrammatic representation of the tensiometer array placed along a representative drainage element in Longlands Field.

Since water moves from high potential to low potential, knowledge of the potential field around a representative drainage element allows the direction of water movement to be determined. If the moisture content of the soil is measured at the same time at the depth of the tensiometers then soil water release curves can be drawn for each of the soil depths. These curves then give the water storage capacity, and some idea of the pore size distribution of the soil.

3.2.5 *Gammarus Pulex* Bioassay

During the course of the project, MAFF fisheries laboratory, Burnham-on-Crouch ran an *in situ* bioassay in the Rosemaund stream at site 1. The bioassay was designed to study changes in feeding rate of the gammarid amphipod crustacean *Gammarus Pulex* in the weeks

following pesticide application, when the organism would be subjected to pulses of pesticide runoff. A number of animals (usually 100) were allocated to individual cages which were placed in holding baskets and deployed in the Rosemaund stream. Each animal was provided with a leaf disc of known weight as a food source. The animals were maintained on site for period of several weeks during which time leaf discs and dead animals were replaced weekly, and uneaten leaf weights measured. Full details of the procedures followed can be found in Matthiessen *et al.* (1993).

3.3 Laboratory Methods

The samples taken by the different research institutes were analyzed by different laboratories. These were generally in-house facilities or laboratories closely controlled by the main funding bodies. In the case of the soil samples these were contracted out to commercial laboratories. While each laboratory had its own detailed methods of analysis, these were based on the so called "Blue Book" methods, (Standing Committee of Analysts, 1985), and Good Laboratory Practice (GLP) was followed throughout.

Pesticide analysis at the low levels experienced in the environment is notoriously difficult and analysis being carried out by a number of laboratories is an added complication. In order to cross check between laboratories and hence give more confidence to the use of the data as a unified whole, two inter-laboratory calibration exercises were carried out. The exercises only involved water samples and were organized by the Building Research Establishment. The laboratories included in the exercises were, University of Birmingham (MAFF samples), NRA Welsh Region (IH samples), IH and MAFF pesticide Laboratory (first year only), Cambridge. The MAFF Cambridge laboratory was not involved in any Rosemaund analysis but was included as a well respected outside control.

The results of the exercises were generally satisfactory in that they showed an acceptable level of agreement between laboratories. The first exercise also highlighted an error in a method for mecoprop being used by one laboratory. Although an amended method proved to be satisfactory it was not possible to reanalyse mecoprop samples taken during the 1990/91 season. Although a great deal of potentially interesting data was lost, at least wrong conclusions on mecoprop mobility were not drawn on faulty data. Details of the methods employed in the inter-calibration exercises and the full results can be obtained elsewhere (Hack, 1992).

During the course of the study the chemical analysis of IH collected samples has been carried out in three different laboratories. Initially, when the study was funded by the DoE, analysis was carried out at the WWA laboratories at Bridgend, subsequently the work was transferred to the NRA laboratory, Llanelli upon its formation in April 1990. The changeover lead to some difficulties given the different operating procedures of the two laboratories and the equipment available. Finally from February 1992 analysis was undertaken by the IH laboratories. Initially this was to cover a gap created by delays in the NRA agreeing to fund an extension to the project. Subsequently the IH laboratories offered the analysis suite required in the numbers necessary for the project.

3.3.1 Bed Sediments

The bed sediments arrived at IFE River Laboratory frozen and were allowed to thaw. Samples that were coarse in nature were sieved through a 2 mm stainless steel sieve. The samples were then frozen overnight and then freeze-dried overnight. The samples were lightly crushed and stored under nitrogen gas in the dark at around 5 °C prior to analysis. The samples were later extracted and analyzed by standard procedures described elsewhere (House *et al.*, 1992; House and Ou, 1992).

3.3.2 Suspended Solids

The water samples were stored in the dark at 5 °C and separated as soon as possible after arrival. The suspended solids were separated by a procedure described previously (House and Ou, 1992). The pesticides in the water samples were extracted with dichloromethane (DCM). The suspended solids were collected on GF/F glass microfibre pads, nominally 0.7 µm pore size: the filters had been pre-treated to remove organic carbon by heating to 520 °C overnight. The filters were placed in soxhlet extraction thimbles, frozen overnight and then freeze dried overnight prior to soxhlet extraction in DCM. The extracts were then concentrated by solvent exchange using the same methods employed for preparation of the bed sediments. All weights were noted to enable the calculation of the suspended solids concentration in µg/l in the aqueous phase and µg/kg (dry weight) for solids.

3.4 Pesticides Studied

In a typical agricultural enterprise a large number of different pesticides are used in the normal run of crop production This is particularly true of an experimental farm such as ADAS Rosemaund, where a great number of agricultural trials are undertaken. It was not practicable to consider carrying out analyses for every pesticide applied and a decision was made, in principle, to concentrate on four chemicals each year, two in autumn and two in spring. A likely list of pesticides was drawn up at the start of the study by the collaborators using the following criteria:

- include some of the most commonly used pesticides,
- choose pesticides that represented a range of the chemical groups (eg phenoxy acids, ureas),
- pesticides chosen should have a range of physico-chemical properties,
- analytical methods should be available for low concentration determinations,
- applications rates were sufficiently high to make leaching possible at detectable levels,
- the chemicals must fit in with the normal crop rotation employed at ADAS Rosemaund.

The chemicals chosen for each year of the study, including comments on the reasons for the choices made, are given in Table 3.2. Some chemicals were monitored in more than one crop year, most notably isoproturon and simazine. This was done primarily in order to build up experience with individual chemicals under changing hydrological conditions. Isoproturon was of interest due to its large usage and its increasing occurrence in surface waters. Simazine,

although not a widely used chemical agriculturally, is used at Rosemaund annually on hops and is easily analyzed. The physico-chemical properties of the chemicals included in Table 3.2 are given in Table 3.3. Finally it should be noted that not all the chemicals listed in Table 3.2 were analyzed by all the bodies involved in the study, usually due either to work load or to no established method being available at a given laboratory.

Table 3.2 Chemicals monitored during the Rosemaund Pesticide Runoff Study.

Cropping Year	Season	Pesticide	Comments
1987/88	Autumn	Mecoprop, Dicamba, 2,4-D	Phenoxy acids, low sorption, mecoprop widely used.
	Spring	Simazine*	Triazine herbicide, moderately sorbed and persistent.
1988/89	Autumn	Simazine, Triclopyr*, 2,4-D*	Triclopyr pyridyloxy herbicide (in the 2,4-D formulation)
	Spring	Simazine*	
1989/90	Autumn	Isoproturon*, Lindane	Isoproturon (urea herbicide) widely used. Lindane (organochlorine insecticide) persistent and sorbed.
	Spring	Mecoprop*, Dichlorprop*	Dichlorprop phenoxy herbicide.
1990/91	Autumn	Isoproturon, Dimethoate, Simazine	Dimethoate, organophosphorous insecticide with short half life and low sorption.
	Spring	MCPA*, Oxydemeton-Methyl, Simazine	Oxydemeton organophosphorous insecticide.
1991/92	Autumn	Atrazine, Carbofuran	Carbofuran and aldicarb, carbamate insecticides.
	Spring	Aldecarb, Simazine*, Atrazine	
1992/93	Autumn	Trifluralin, Isoproturon, Deltamethrin	Trifluralin (dinitro aniline herbicide) and Deltamethrin (pyrethroid insecticide) both strongly sorbed*.
	Spring	Fenpropimorph, Chlorpyrifos	Morpholine fungicide and organophosphorous insecticide both strongly sorbed.

* Only analyzed by IH/NRA, * only analyzed by MAFF.
* Sorption coefficient and half life are given in Table 3.3.

Table 3.3 **Physico-chemical properties of the chemicals monitored during the course of the Rosemaund Runoff Study.**

Chemical	Half Life[#] (days)	Koc[#] (ml/g)
Mecoprop	21.0	20.0
Dicamba	14.0	2.0
2,4-D	10.0	20.0
Simazine	60.0	130.0
Isoproturon	12.0-29.0[+]	130.0
Triclopyr	46.0[+]	126.0[+]
Lindane	400.0	1100.0
Dichlorprop	10.0	1000.0
Dimethoate	7.0	20.0
MCPA	25.0	20.0
Oxydemeton-methyl	10.0	10.0
Atrazine	60.0	100.0
Carbofuran	50.0	22.0
Aldicarb	30.0	30.0
Trifluralin	60.0	8000.0
Deltamethrin	2.0-5.0[+]	110000.0[*]
Fenpropimorph	15.0-93.0	4715.0[*]
Chlorpyrifos	30.0	6070.0

\# K_{oc} describes the distribution of a pesticide between the soil water and soil organic carbon phases. Values from Wauchope et al, 1992 unless indicated

\+ Agrochemicals Handbook, 3rd Edition

* Calculated from Karichoff 1981, $K_{oc} = 0.41\ K_{ow}$, where K_{ow} describes the distribution of the pesticide between octan-1-ol and water (determined in the laboratory).

4. RESULTS

4.1 Soil Hydrology

The study of the soil hydrology of the Rosemaund catchment was a major piece of work carried out by the Agrohydrology section of IH funded through its own science budget research programme. Two internal reports have been written (Bell *et al*, 1990, 1991) that give detailed information on the season by season changes in the soil water pathways as observed over the first two years of the study. A summary of the finding are given here as a help to explaining the results of the pesticide monitoring study (Section 4.2) and forming the basis of the pesticide model (Section 5.2).

4.1.1 Macropores

The hydrological role of macropores in these soils is crucial. Because the conductivity of the soil matrix is so low, it is the macropores that form the dominant flow pathways within the soil. A macropore may be defined loosely as a planar or tubular pore which traverses the soil and which is created by a secondary influence (eg earth worms). It may be 'blind' ie. not joined to another macropore, or it may be part of an interconnected plexus; both have important roles in these soils. Being larger than most of the soil pores of the soil matrix (eg. anything from about 0.1 mm to 10 cm) these openings have the potential to conduct water freely, but are only able to do so if the soil water potentials are very high (close to, or at, saturation) or if water, ponded elsewhere, is able to pour down them at a rate exceeding that of the adjoining matrix to absorb it.

A distinction needs to be made between two types of macropore. One type is created by the shrink/swell process, and varies in size and depth of penetration according to the soil water content. These largely (but perhaps not totally) close during winter due to swelling of the soil. They form a pathway for rapid bypass flow at times where they are open, but only to saturated or quasi-saturated flow. Ponding of water somewhere in or on the soil profile is necessary before they conduct, but once such conditions are established, large amounts of flow can be accommodated, albeit for short periods. This flow may be downwards to feed the groundwater system where shrinkage cracks have penetrated to join the geological system, or lateral 'interflow' down-slope to the valley bottom. These cracks form a considerable proportion of the volume of the dry soil, and these also act as a quick-fill reservoir to hold water and thus facilitate the re-wetting of the lower soil surface. The fate of pesticides in these circumstances would be very different.

The second type of macropore is created by biological activity, mainly that of worms, but some also are due to dead root holes. These seem to remain active throughout the winter period and provide the otherwise poorly conductive soil with an enhanced saturated conductivity which it otherwise would not have. Worm activity is largely concentrated in the upper soil during winter and is probably responsible for such lateral flow as there is from the mid-drain zone towards the drains. It seems likely that the presence of the drains encourages worm activity in that zone due to lower water tables and better aeration, and this may explain the differences in behaviour of the mid-drain zone and the drain zone.

4.1.2 Summary of the annual cycle

For simplicity the annual cycle has been divided into four stages: stage 1 will be referred to as 'the summer phase', stage 2 as 'the soil re-wetting phase', stage 3 as 'the drainage phase' and stage 4 as the 'crop abstraction phase'.

The Summer Phase

The summer phase is characterised by progressive downward drying of the soil as the rooting zone of the crop advances and demand increases. This is accompanied by development of an intricate network of shrinkage cracks, dividing the soil into irregular 'peds', 50-75 cm across.

The summer of 1990 was exceptionally dry and the cracks penetrated to 1 m at least, where they almost certainly became linked to the joint system in the underlying geological formation below about 1 metre - soft, compact, blocky, silty mudstone. However, in wetter summers, this may not necessarily be so. When the soil re-wets, such cracks obviously re-swell and close, although not necessarily completely. The data taken as a whole suggest that residual cracks may persist throughout the entire winter, unless disturbed by ploughing, albeit at a much lower conductivity.

The Soil Re-wetting Phase

In general, autumn re-wetting will be controlled by the timing and characteristics of autumn rainfall and by the timing of cultivation in relation to these. The re-wetting process will probably take one or two distinctly different forms:-

(i) If there is little prolonged heavy autumn rain prior to cultivation, or if the preceding summer was so wet that shrinkage crack development was minimal, events will follow those of 1990/91, with the creation of a persistent wet layer overlying very dry soil.

Autumn-applied pesticides will be introduced into the finer soil pores of this layer, and subsequently would be expected to be less mobile, moving by piston flows, slowly because of the poor conductivity of the actual soil. The duration of this stage will depend on the amount of rain.

(ii) If however, heavy rain occurs early in autumn, preceding cultivation, sufficient in intensity and amount that the dry soil is unable to accept the influx, the resulting surface saturation will run down the cracks and wet up the entire soil profile within a few days. Water movement through the fissures will predominate. This water will go primarily to recharge the shallow aquifer of the underlying geological formation, but if the input rate is high enough, the water table will rise temporarily above drain level in the zone close to the drains, and may be sufficient to produce intermittent pulses of drain flow. It is possible that this is what was observed in the autumn of 1989, but the data set for that period is too limited to compare directly with the autumn of 1990.

The Drainage Phase

Once water tables have generally risen above drain level, normal drainage starts. Water percolates vertically down through the unsaturated zone until it meets the water table, after which it moves laterally as saturated flow, mainly via the macropores along the hydraulic gradient to the drain.

During this phase the vertical gradients of total potential below the water table are as close to zero as can be measured, so unless the saturated conductivity is very high indeed (unlikely) there is no further deep drainage at this stage - the only movement is lateral, and that is entirely in the saturated zone, mainly via the various fissures and joints.

The Crop Abstraction Phase

In most years, by early April, the water demand of the crop starts to exceed the average rain input rate, so that the root zone starts to become drier and a zero flux plane develops beneath it. This zone of upward fluxing water encroaches downwards into the zone beneath as the roots advance and deplete the water reserves of the upper layers. This 'soil moisture deficit' acts as a barrier to further inputs of rain to the lower profiles, with the result that the water table recedes to below the drains level into the geological formation. Drainflow is impossible under these conditions and will not start again until the next winter. The cycle is completed with the return to the summer phase.

4.1.3 Down-slope saturated flow through the aquifer

Much of the saturated flow beneath the water table converges on the drain and soon exits at the outfall. However, it must be remembered that there is a topographic effect which has not yet been discussed. The field has an average slope of about 6%, the water table overall can be expected to conform to this gradient, subject to localised troughs corresponding to the lines of the field drains. This implies that there will be an un-quantified but fairly constant lateral flow below drain level within the geological formation, presumably to exit as 'base flow' at the valley bottom.

While it seems that most of the conductivity of these soils and the underlying geology is derived from the cracks and joints, it must be noted that the water holding capacity of these pathways is very small - probably much less than 1% of the soil volume. This is clear from the soil water content data of 1989/90, which show a marked difference between the soil of the upper metre and the geological material below 1 m (Fig. 4.1). Thus, the velocity of the water passing through these pathways must be relatively high.

4.1.4 Summary of Soil Water Pathways

Almost all the fields in ADAS Rosemaund are underdrained and therefore it is possible to generalize the observations made from the soil water the entire catchment. This is best done by considering a representative drainage element. This is the part of a field that extends from

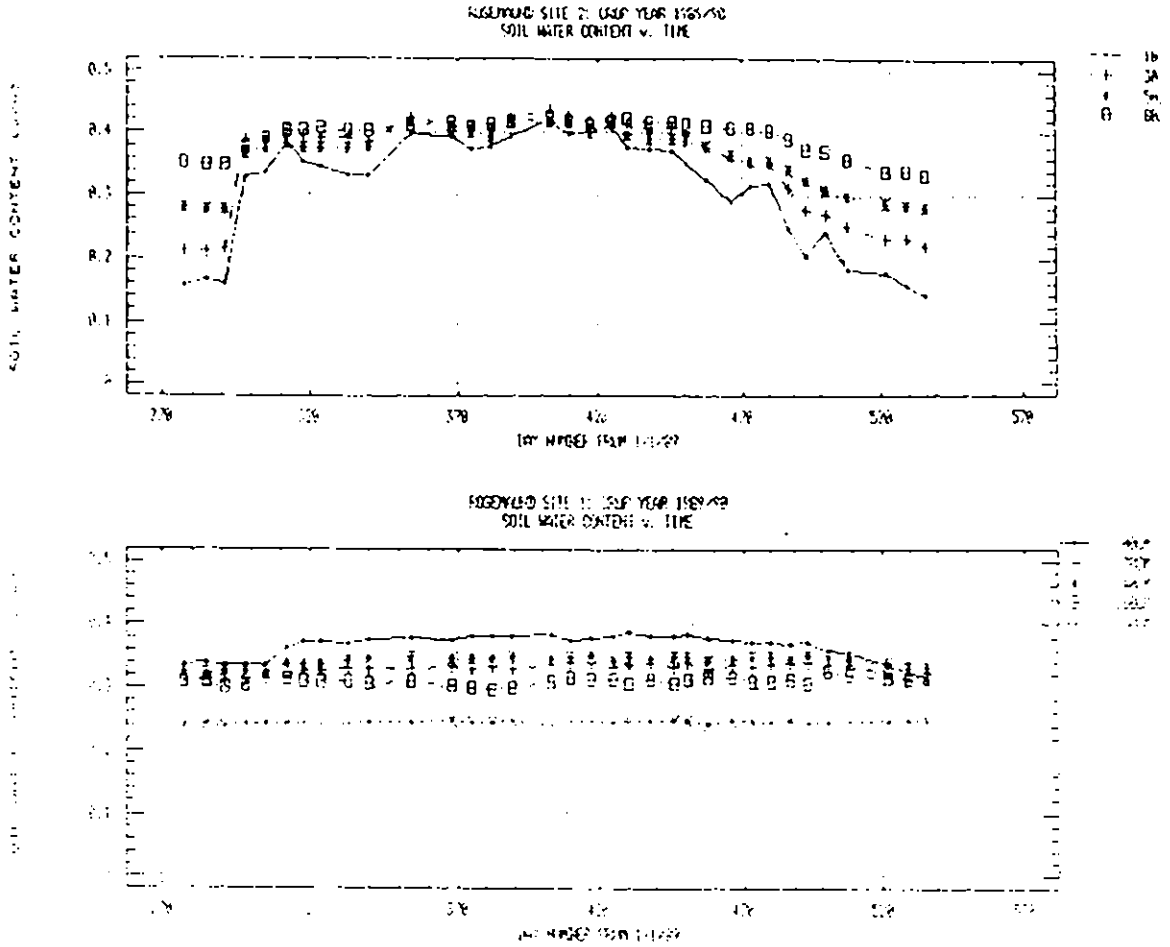

Figure 4.1 Soil water content variation, 1989/90, for soil layer (0 to 80 cm) and geological parent material below (100 to 180 cm).

one mid-drain position to the next, a distance of 20 m. The component parts of this drainage element are shown in Figure 4.2. The soil profile can be divided into three horizons; (a) a moderately conductive topsoil with many macro-pores, (b) an almost non-conducting subsoil with fewer macro-pores, and (c) a blocky structured parent material (geology) in which any water movement is confined to macro-pore flow. Superimposed on this vertical structure is a horizontal division between the area around the drain (drain zone) and the inter-drain zone. The drain zone is characterized by high conductivities and high macro-pore density. The inter-drain area has a very low, near zero, permeability, with some but much fewer macro-pores.

In the autumn prior to the water table rising above drain level, heavy rainfall may exceed the acceptance potential of the soil surface and flood down the large shrinkage cracks remaining from summer. Such rain falling on the drain zone enters the drain through the backfill due to ponding at the base of the macro-pore zone. Some of this water may pass through the drain

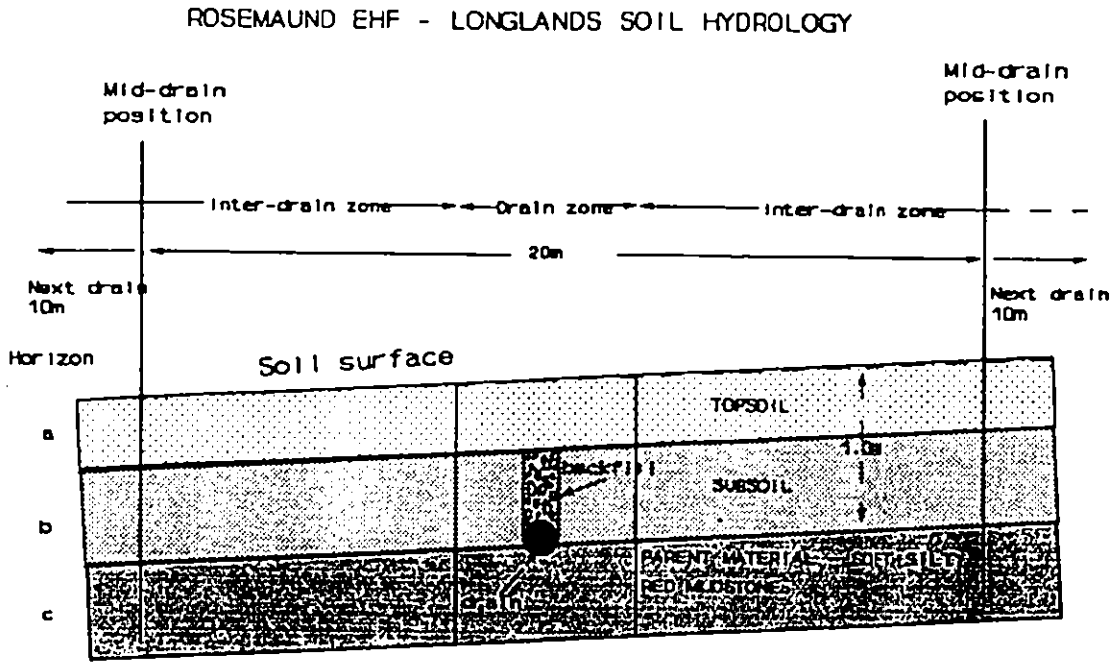

Figure 4.2 Diagram showing the main features of a vertical cross-section through the main hydrological unit affecting soil water movement.

to recharge the groundwater. Water falling on the inter-drain zone is absorbed into the soil peds and probably little of this goes anywhere else. The foregoing process depends on the rainfall being heavy, because prolonged light rain causes shrinkage cracks to close. Cultivation of the topsoil, while destroying the crack structure, will allow lateral movement of water over the impermeable topsoil to the drain zone and hence the drain. Once a water table is established and has risen above the subsoil, rapid lateral movement to the drains will also occur through macro-pores and more slowly through the soil matrix. Thus for modelling purposes the drain and inter-drain zones require separate treatment, which also has to take account of seasonal changes in water table and in soil macro-pore conductivity.

4.2 Pesticides

The objective of this section is to summarize all the pesticide runoff data that has been collected during the monitoring exercise carried out at ADAS Rosemaund. In the discussion of the results pesticide data collected by MAFF will also be included where appropriate. Data presented from sites 0 and 5 were collected by IH, and from sites 1 and 3 by MAFF. The discussion will, as far as possible, take the data set as a whole and identify patterns in the pesticide runoff and illustrate this by detailed descriptions of representative plots of pesticide concentrations during rainfall events. This approach has been adopted since it would be impossible to present all the data for all the individual events monitored. Details of all these

events are being published in a series of reports by the Rosemaund Management Steering Group (Bird *et al*, 1991; Hack, 1992).

4.2.1 Pesticide Concentrations and Losses

The pesticide runoff events monitored over the period of the study are summarized, by chemical, in Table 4.1. Details are given of applications made to the catchment areas above each sampling location which were made prior to, or between monitored events. On occasions the monitoring of a particular event did not coincide with the hydrograph. This was mainly due to failure of the automatic trigger mechanism and subsequent manual initiation of sampling. These events are indicated in Table 4.1. Tables 4.2 and 4.3 summarizes the concentrations of all pesticides monitored in the routine samples that were taken from the main gauging station at site 0 and the outlet from the drainage system under Longlands Field, site 5.

Table 4.1 Summary of pesticide applications and subsequent runoff data collected as a result of rainfall events during the Rosemaund Study

	Application				Rainfall							
Compound	Date	Rate[1] (kg/ha)	Area[2] (ha)	Amount (kg)	Date	Amount (mm)	Lag[3] (days)	Src[4]	Max. conc. (µg/l)	Mean conc.[4] (µg/l)	Mass Out (g)	L[5]
Dicamba	20/11/87	0.425	5.200	2.21	+16/12/87	9.0	26	1	0.60	0.45	0.053	0.017
			5.200	2.21	+16/12/87	9.0	26	0	2.26	1.176		0.004
	08/12/88	0.255	5.200	1.33	024/02/89	13.5	78	1	<0.01	<0.01		0.001
Dichlorprop	20/03/90	2.600	5.200	13.52	19/05/90	12.0	60	1	1.00	0.35	0.021	0.053
Isoproturon	01/11/89	1.000	2.140	2.14	18/11/89	28.5	7	3	8.40	4.30	0.12	0.358
			2.140	2.14	09/11/89	10.5	8	3	13.70	6.70	0.15	0.351
	17/11/89	0.375	3.060	1.15			26	3				
			2.140	2.14	13/12/89	52.5	42	3	8.80	3.20	0.76	0.309
			5.200	5.20			42	1				
			10.800	4.05	13/12/89	52.5	26	1	5.00	3.30	3.8	0.131
	11/10/90	1.000	10.800	10.80			75	1				
	28/11/90	1.900	5.200	9.88	25/12/90	10.5	27	1	17.20	10.60	0.9	0.230
			10.800	10.80			89	1				
			5.200	9.88	08/01/91	15.0	41	1	2.62	0.96	0.52	0.174
			3.060	3.06			89	3				
			2.140	4.07	08/01/91	15.0	41	3	12.10	#3.54		0.444
			0.000	0.00			89	5				
			2.000	3.80	08/01/91	15.0	41	5	0.58	0.14	0.001	0.837
			10.800	10.80			133	1				
			5.200	9.88	21/02/91	11.5	85	1	2.10	0.92	0.4	0.072
			0.000	0.00			133	5				
			2.000	3.80	21/02/91	11.5	85	5	2.70	1.40	0.21	0.347
			0.000	0.00			144	5				
			2.000	3.80	04/03/91	12.0	96	5	2.50	#1.70		0.279
			10.800	10.80			75	0				
			5.200	9.88			27	0				

Compound	Application Date	Rate[1] (kg/ha)	Area[2] (ha)	Amount (kg)	Rainfall Date	Amount (mm)	Lag[3] (days)	Site[4]	Max. conc. (µg/l)	Mean conc.[5] (µg/l)	Mass Out (g)	L[5]
	13/10/90	1.000	5.000	5.00			73	0				
	06/11/90	0.500	23.400	11.70	25/12/90	10.5	49	0	1.76	0.49	0.51	0.091
			10.800	10.80			86	0				
			5.200	9.88			38	0				
			5.000	5.00			84	0				
			23.400	11.70	05/01/91	9.5	60	0	5.20	0.36	0.65	0.073
			10.800	10.80			89	0				
			5.200	9.88			41	0				
			5.000	5.00			87	0				
			23.400	11.70	08/01/91	15.0	63	0	6.70	#0.60	-	0.069
			10.800	10.80			133	0				
			5.200	9.88			85	0				
			5.000	5.00			131	0				
			23.400	11.70	21/02/91	11.5	107	0	<0.02	<0.02	-	0.028
			10.800	10.80			156	0				
			5.200	9.88			108	0				
			5.000	5.00			154	0				
			23.400	11.70	16/03/91	10.0	130	0	16.20			0.018
	30/10/91	0.500	5.500	2.75			49					
	30/11/91	0.500	4.000	2.00			18					
	04/12/91	0.500	12.200	6.10			14					
	05/12/91	0.500	5.000	2.50	18/12/91	5.5	13	0	15.10	6.12	0.24	0.063
			5.500	2.75			211					
			4.000	2.00			180					
			12.200	6.10			176					
			5.000	2.50			175					
	27/12/91	0.500	18.000	9.00	28/05/92	5.5	153	0	7.80	4.82	3.6	0.005
			5.500	2.75			221					
			4.000	2.00			190					
			12.200	6.10			186					
			5.000	2.50			185					
			18.000	9.00			163					
	03/06/92	1.500	2.000	3.00	07/06/92	5.5	4	0	10.00	4.39	2.1	0.024
Lindane	01/11/89	0.560	2.140	1.20	08/11/89	28.5	7	3	4.50	1.20	0.007	0.228
			2.000	1.12	08/11/89	28.5	7	5	1.90	#0.85	-	0.553
			2.140	1.20	09/11/89	10.5	8	3	4.10	1.20	0.027	0.227
			2.140	1.20	13/12/89	24.0	42	3	0.45	0.14	0.004	0.214
			5.200	2.91	14/12/89	18.0	43	1	0.29	0.12	0.16	0.076
			2.000	1.12	*15/12/89	40.0	44	5	2.55	#0.57	-	0.519
			5.200	2.91	*15/12/89	40.0	44	0	0.75	#0.16	-	0.076
			2.140	1.20	19/03/90	9.0	138	3	0.03	0.01	0.00008	0.181
			5.200	2.91	19/03/90	9.0	138	1	<0.02	0.01	0.0007	0.064
Mecoprop	17/11/87	2.000	5.500	11.00	19/11/87	25.0	2	1	11.70	4.20	7.5	0.288
			5.500	11.00	+20/11/87	25.0	3	0	0.12	0.04	0.04	0.066
			5.500	11.00	+16/12/87	11.5	29	0	1.57	0.84	1	0.028
			5.500	11.00	+16/12/87	11.5	29	1	<0.01	<0.01	-	0.811
	22/03/90	0.650	10.800	7.02	15/05/90	12.0	54	1	1.40	0.30	0.019	0.033
Simazine	02/03/88	1.700	4.120	7.00			91	0				
	05/03/88	1.700	3.760	6.39	01/06/88	16.5	88	0	1.83	0.93	0.25	0.031
	08/12/88	1.150	6.000	6.90	24/02/89	13.5	78	1	1.80	0.50	0.3	0.078
			6.000	6.90			78	0				

	Application				Rainfall							
Compound	Date	Rate[1] (kg/ha)	Area[2] (ha)	Amount (kg)	Date	Amount (mm)	Lag[3] (days)	Sec[4]	Max. conc. (µg/l)	Mean conc.[4] (µg/l)	Mass Out (g)	L[5]
	16/02/89	1.700	4.120	7.00			8	0				
	17/02/89	1.700	3.760	6.39	24/02/89	13.5	7	0	68.00	22.40	60.6	0.100
			6.000	6.90			84	0				
			4.120	7.00			14	0				
			3.760	6.39	02/03/89	10.5	13	0	15.70	8.20	9.2	0.093
	23/11/90	1.200	3.760	4.51	25/12/90	10.5	32	0	4.12	1.70	1.77	0.021
			3.760	4.51	05/01/91	9.5	43	0	1.50	0.90	1.6	0.018
			3.760	4.51	08/01/91	20.5	46	0	0.84	#0.49	-	0.019
			3.760	4.51	21/02/91	11.5	90	0	0.36	0.26	1.25	0.011
			3.760	4.51			113	0				
	02/03/91	1.700	4.850	8.25	16/03/91	9.5	14	0	15.30	3.30	11.8	0.054
Triclopyr	08/12/88	0.195	5.180	1.01	24/02/89	13.5	78	1	<0.01	<0.01	-	0.009
2,4-D	20/11/87	1.000	5.180	5.18	20/11/87	9.0	0	0	0.15	0.06	-	0.034
			5.180	5.18	16/12/87	9.0	26	0	5.12	2.57	3.2	0.006
			5.180	5.18	16/12/87	9.0	26	1	1.00	0.71	0.09	0.024
	08/12/88	0.600	5.120	3.07	24/02/89	13.5	78	1	<0.01	<0.01	-	0.000
Dimethoate	28/11/90	0.300	16.000	4.80	25/12/90	10.5	27	1	3.05	1.20	0.1	0.009
			16.000	4.80	08/01/91	15.0	41	1	0.22	0.03	0.031	0.002
			5.200	1.56	08/01/91	15.0	41	3	0.58	#0.22	-	0.005
			2.000	0.60	08/01/91	15.0	41	5	<0.02	<0.02	-	0.005
			2.000	0.60	21/02/91	11.5	85	5	<0.02	<0.02	-	0.000
			2.000	0.60	04/03/91	12.0	96	5	<0.02	<0.02	-	0.000
Atrazine	27/11/91	2.800	5.200	14.56	18/12/91	5.0	21	0	1.76	0.60	0.02	0.080
			2.000	5.60	05/01/92	4.0	39	5	56.50	35.70	0.085	1.785
			5.200	14.56	08/01/92	72.5	42	1	5.70	2.00	9.9	0.251
			2.140	5.99	08/01/92	72.5	42	3	51.30	10.60	13.5	0.708
			2.000	5.60	08/01/92	72.5	42	5	81.40	15.90	4.79	1.724
			5.200	14.56	08/01/92	72.5	42	0	0.37	0.23	0.39	0.063
			5.200	14.56	25/01/92	9.0	59	1	49.40	1.90	0.15	0.206
			2.140	5.99	25/01/92	9.0	59	3	58.40	5.70	0.013	0.582
			5.200	14.56	14/04/92	17.5	139	1	2.40	0.11	0.009	0.082
			2.140	5.99	14/04/92	17.5	139	3	9.90	0.45	0.005	0.231
			2.000	5.60	14/04/92	17.5	139	5	16.20	11.20	0.022	0.562
			5.200	14.56	28/05/92	14.5	183	1	0.02	0.06	0.004	0.049
			2.140	5.99	28/05/92	14.5	183	3	0.18	1.60	0.001	0.139
			5.200	14.56	28/05/92	14.5	183	0				
	02/05/92	1.00	8.000	8.00	28/05/92	14.5	26	0	1.76	0.90	0.83	0.054
			5.200	14.56	07/06/92	14.5	193	0				
			8.000	8.00	07/06/92	8.0	36	0	3.00	1.07	0.53	0.048
Carbofuran	03/12/91	3.00	3.000	9.00	18/12/91	5.5	15	0	35.50	3.77	0.15	0.051
			3.000	9.00	08/01/92	72.5	36	0	<1.00	<1.00	-	0.038
			3.000	9.00	08/01/92	72.5	36	1	26.80	10.40	52.6	0.153
			1.000	3.00	08/01/92	72.5	36	3	264.00	25.70	32.8	0.350
			3.000	9.00	25/01/92	9.0	53	1	49.40	6.20	0.49	0.121
			1.000	3.00	25/01/92	9.0	53	3	58.40	37.20	0.09	0.276
			3.000	9.00	14/04/92	17.5	133	1	2.40	0.46	0.038	0.040
			1.000	3.00	14/04/92	17.5	133	3	9.90	1.00	0.011	0.091
			3.000	9.00	28/05/92	28.0	177	1	0.02	0.01	0.0004	0.022
			1.000	3.00	28/05/92	28.0	177	3	0.18	0.09	0.00007	0.050
Aldicarb	27/02/92	0.55	2.000	1.10	14/04/92	17.5	47	5	3.15	1.02	0.002	0.186
			4.200	2.31	28/05/92	28.0	91	0	0.21	0.46	0.34	0.002
X			4.200	2.31	7/6/92	8	101					
	05/06/92	1.30	2.000	1.10	10/06/92	Lac	2	0	2.84	0.90	0.44	0.009
Triflusulfuron	08/11/92	1.10	2.000	2.20	11/11/92	10.5	3	5	14.12	3.49	0.032	1.063
			2.000	2.20	14/11/92	5.0	6	5	2.20	0.39	0.01	1.026

		Application			Rainfall							
Compound	Date	Rate[1] (kg/ha)	Area[2] (ha)	Amount (kg)	Date	Amount (mm)	Lag[3] (days)	Site[6]	Max. conc. (µg/l)	Mean conc.[4] (µg/l)	Mass Out (g)	L[5]
			2.000	2.20	25/11/92	17.5	17	5	1.00	0.72	0.011	0.904
MCPA	28/02/91	1.68	16.000	26.88	04/03/91	15.5	4	1	12.44	1.92	0.096	0.674
			5.210	8.75	04/03/91	15.5	4	3	18.80	5.40	0.33	1.504
			16.000	26.88	03/07/91	26.5	7	1	1.98	1.20	0.29	0.620
			16.000	26.88	16/03/91	10.0	16	1	6.00	1.90	0.72	0.483
			5.210	8.75	+19/03/91	11.0	19	3	46.80	14.60	0.70	0.992

Notes:
1. Application rate of active ingredient.
2. Area treated draining to the sampling point.
3. Time in days between application date and rainfall event.
4. Flow weighted mean concentration (unless otherwise indicated).
5. Index of mass available for transport, see Section 4.1.1.
6. See Figure 3.2 for locations.
\# Simple mean, no flow data available.
\+ Chemical sampling missed main hydrograph.
* Multiple events captured with longer sampling interval.

Defining an event as a concentration profile of a single pesticide through a hydrograph at a given location, then 93 such events were monitored in the course of the study. Of these 93 events in only nine cases was the concentration of pesticide below the detection limit. In 80 of the events the maximum concentration was greater than the MAC level for drinking water laid down by the EC, this number falls to 76 if the flow weighted mean concentration is used as the criteria.

In general, when pesticide was applied to a field draining to both a drainage system and the stream, the higher concentrations were found in the drain. This is because usually all the catchment area of the drainage system was treated, while the stream concentration could be diluted with water from untreated areas. The maximum concentration of any pesticide measured during the study was 264.0 µg/l of carbofuran on 8 Jan. 1992 in the drain at site 3. This was in response to a very large rainfall event of 72.5 mm in 25 hours, such an event occurs only once every 50 years. Atrazine concentrations were also measured in the same event at drain sites 3 and 5. These were again high with maximum concentrations of 51.3 µg/l and 81.4 µg/l respectively.

Maximum concentrations over 10 µg/l occurred quite often during the study with 25 events exceeding this value. Peak values in the range 1-10 µg/l occurred in 40 events, while 28 events had peak values of less than 1 µg/l. A more detailed study of those events which gave rise to the lower pesticide peak concentrations reveals several factors which seem to control this behaviour (ignoring those events that missed the hydrograph peak as they may have given un-representatively low concentrations, see Section 4.2.2.). The main factors seem to be the number of half-lives that pass between the application date and the rainfall event, and the fraction of the catchment that is treated. In the dicamba event of 8 Dec. 1988 for example, there is was delay of almost 8 half-lives between application and rainfall event. The atrazine and carbofuran events of 28 May 1992 also occurred several half lives after application. The simazine events of 8 Jan. 1991 and 21 Feb. 1991 followed pesticide applications to only 3.76 ha of a catchment whose total area is some 151 ha. The triclopyr data demonstrated the effect

of combining a low application rate to a small area of a large catchment with three half-lives between application and rainfall event. The lindane events occurring after November 1989 nearly all show low peak concentrations. While the latter two events occurred many days after application it was not a long time compared to its quoted half life of 400 days. However measurement of soil residues by BRE (Williams *et al*, 1991), show that the real half life in the field was closer to 40 days.

It seems therefore that consideration of the physico-chemical properties of the chemical combined with knowledge of the amount and area of treatment can indicate expected peak concentrations in surface waters as they are influenced by the timing of a rainfall events. Based on this evidence an attempt has been made to develop an index of pesticide runoff based on the data in Table 4.2. The calculation of the index and a discussion of its success is given in Section 4.2.4.

While the maximum concentrations of a pesticide is the standard by which the quality of an agricultural non-point source is judged, the actual amount of runoff is also of considerable interest. Table 4.1 gives the results of calculating the mass of pesticide passing each sampling point in each event. In the majority of cases the amounts were very small with the most being below 1 g. The highest recorded loss was 60.6 g of simazine recorded at site 0 in spring 1989, which represented 0.3 % of the total applied to the catchment. The highest cumulative runoff of pesticide recorded was 1.1 % of the total applied and was measured in the water leaving the drain at site 3, following an application of carbofuran. When compared to the application rates these small mass losses of pesticide may seem trivial, however, they give rise to very high concentrations albeit for short lengths of time. It would seem almost impossible to prevent any chemical deliberately introduced into the environment, as is the case with pesticides from, reaching surface waters in such small amounts, whatever the method of application and agricultural practice used.

Table 4.2 Summary of pesticide concentrations measured in routine (not event) samples taken from the main gauging site, site 0.

Pesticide	Concentration (µg/l)			
	Mean[1]	Minimum	Maximum	No. of Samples (No. below detection limit)
Lindane	-	< 0.005	0.12	31(26)
Isoproturon	8.4	< 0.02	27.8	42(1)
Atrazine	1.2	< 0.01	19.0	84(1)
Simazine	0.8	< 0.01	7.2	84(6)
Dimethoate	-	< 0.005	<0.02	17(17)
Oxydemeton-methyl	-	< 10.0	< 10.0	17(17)
Carbofuran	-	< 0.1	9.3	9(6)
Aldicarb	-	< 0.02	< 0.2	11(11)
Sulphoxide	-	< 0.15	< 0.15	3(3)
Sulphone	-	< 0.05	0.07	3(2)
Trifluralin	-	< 0.08	0.17	7(6)

Notes: 1. Concentrations less than detection limit are assumed to be half detection limit in calculating the mean.

Table 4.3 Summary of pesticide concentrations in routine (not event) samples taken from Longlands Drain, Site 5.

Pesticide	Concentration (µg/l)			
	Mean[1]	Minimum	Maximum	No. of Samples (No. below detection limit)
Lindane	-	< 0.005	0.01	7(7)
Isoproturon	17.8	< 0.02	112.0	16(8)
Atrazine	11.7	< 0.01	160.0	18(9)
Simazine	0.2	< 0.01	2.1	17(7)
Dimethoate	-	< 0.02	<0.02	5(5)
Oxydemeton-methyl	-	< 10.0	< 10.0	5(5)
Carbofuran	-	< 1.0	< 1.0	2(2)
Trifluralin	0.6	< 0.08	1.73	7(3)

Notes: 1. Concentrations less than detection limit are assumed to be half detection limit in calculating the mean.

4.2.2 Patterns of Pesticide Runoff

This section examines in more detail the way in which pesticide concentrations relate to rainfall and flowrate for individual events. The shapes of the pesticide concentration curves can be divided into three main types:

1) those which showed no obvious pattern at all,
2) those when the peak value occurred at the start of monitoring,
3) those which showed a dilution in concentration through the hydrograph and subsequent return to base levels.

The majority of events fall into group 2, while there are a significant number in group 1. The pesticide concentrations showing least pattern generally occur at the main gauging site and reflect the greater variety and lengths of pesticide pathway that operate at the catchment scale compared to those operating at the field scale. The following discussion will deal with each of these three groups, for ease of reference they will be identified as type 1, type 2 and type 3 events respectively.

Type 1 events

This type of pesticide response to rainfall events accounts for only about 10 % of the events observed. As was stated above the majority of these were monitored at the outlet from the farm catchment at site 0. Two examples should be sufficient to illustrate this type. Figure 4.3 shows isoproturon concentrations at site 0 following 10.0 mm of rainfall, the applications having been made over the period 16 Oct. 1990 to 28 Nov. 1990 (see Table 4.1). The flow response to the rainfall is as expected, however the two distinct isoproturon peaks show no correlation to either rainfall or flow. Figure 4.4 shows a similar lack of correlation between, in this case, atrazine, rainfall and flow. Here a single application of atrazine was made some 21 days before a small rainfall event which occurred on 17 Dec. 1991 (see Table 4.2). Although the atrazine concentration did seem to reach a peak during the recession limb in the hydrograph there is no apparent reason why it should lag the peak flow by approximately 12 hours.

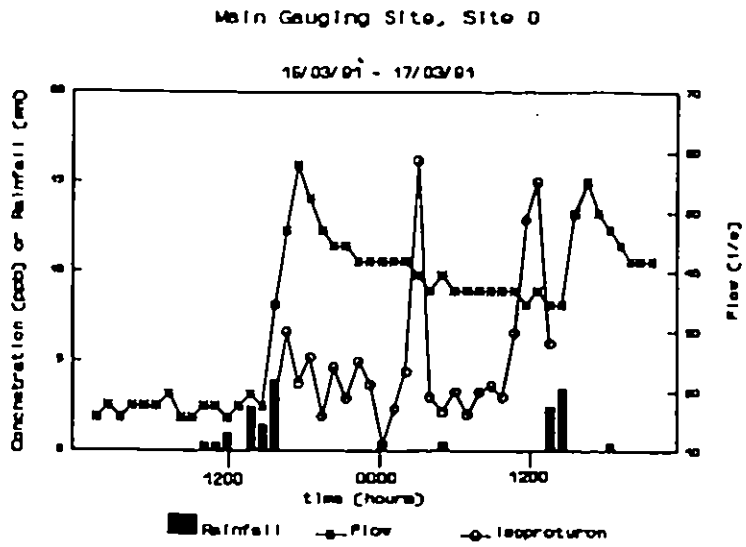

Figure 4.3 **Isoproturon concentrations in the stream draining ADAS Rosemaund following a rainfall event.**

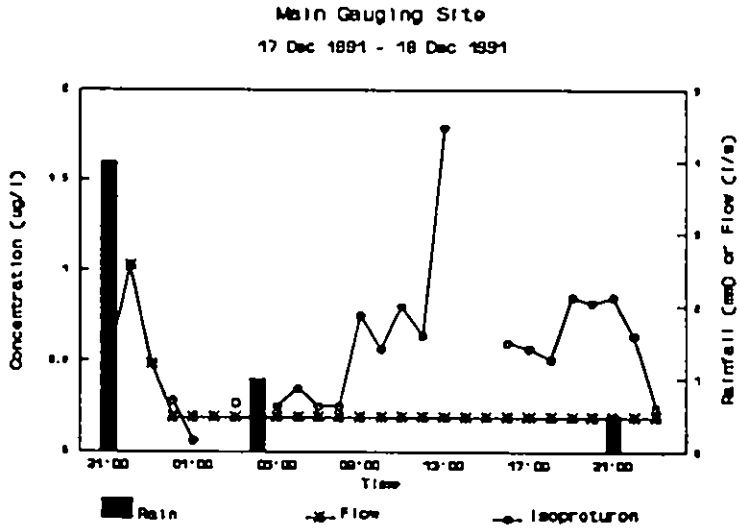

Figure 4.4 **Atrazine concentrations in the stream draining ADAS Rosemaund following a rainfall event.**

Type 2 events

In this type of event rainfall produces a corresponding peak in pesticides concentration in the stream or drainage water. The pesticide peak may either occur shortly before the peak in the hydrograph or coincide with it. This type of event formed the majority (approximately 80%) of those monitored at Rosemaund. Figures 4.5 and 4.6 are excellent examples of this type of event. Both graphs show the change in simazine concentrations at site 0 resulting from a rainfall event which occurred shortly after pesticide application (see Table 4.1 for details). In both cases the peak simazine concentration occurred before the hydrograph peak, the concentrations then fell off rapidly through the peak and recession of the hydrograph. It is

interesting to note that this is the same event as shown in Figure 4.3 that produced a Type 1 response for isoproturon. A slightly different response is shown in Figure 4.7 also for simazine concentrations following a recent application. Here the rain fell over two close but separate periods, the first rainfall causing a simazine peak slightly after the hydrograph peak, and the second rainfall giving rise to a coincidence of the pesticide and hydrograph maxima.

This type of response was not confined to simazine. Figure 4.8 shows the change in the concentration of the breakdown products of aldicarb in the drainage water from Longlands field. In this case, due to a build up in the soil moisture deficit, the rainfall event produced only a small change in drain flow. However the coincidence of pesticide and hydrograph peak is clearly illustrated. A similar response can be seen for trifluralin for the same location and under conditions that gave rise to a very similar hydrological response (Fig. 4.9 and 4.10). This chemical is interesting because it has a very high sorption coefficient yet it behaves similarly to other less sorbed chemicals (see Section 4.2.3).

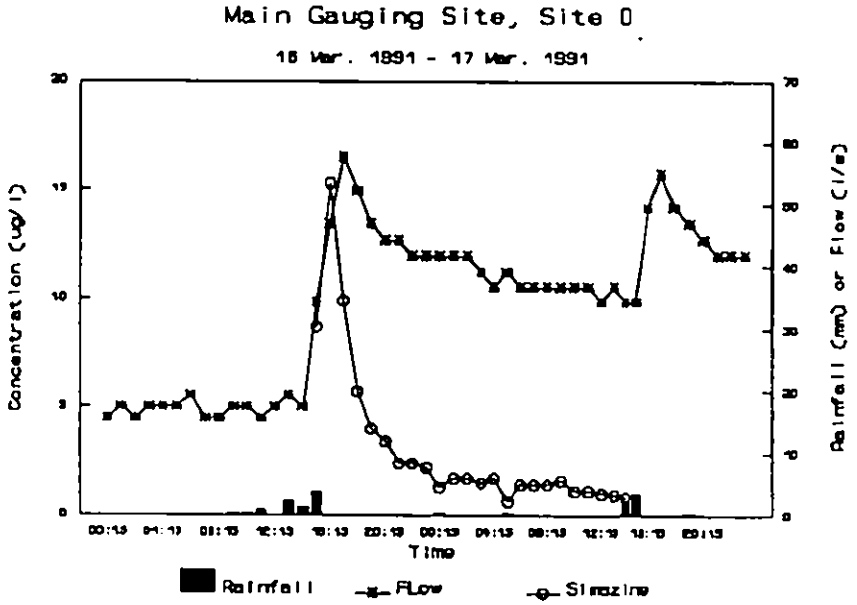

Figure 4.5 Simazine concentrations leaving the Rosemaund catchment following a rainfall event after an application.

There are two possible hypotheses that can be put forward to explain type 2 responses. The first is based on the likelihood that pesticide concentrations do not equilibrate between the dissolved and solid phases instantaneously. When a pesticide is applied to soil some will remain on the soil while some will dissolve into the soil water, the relative concentrations depending on the sorption coefficient for the particular molecule/soil combination. In the initial stages of a rainfall event, the rain displaces the original soil water, which is of high pesticide concentration, and forces it to move down the profile. If there are by-pass routes available then this water will reach the drainage system and hence the stream in a short space of time, thus causing an initial peak pesticide concentration. During the remainder of the event there is insufficient time for full equilibrium to be established between the displacing water and the soil matrix, thus the remaining water moving to the drains is of a lower concentration. Between rainfall events, equilibrium is re-established and so each event starts

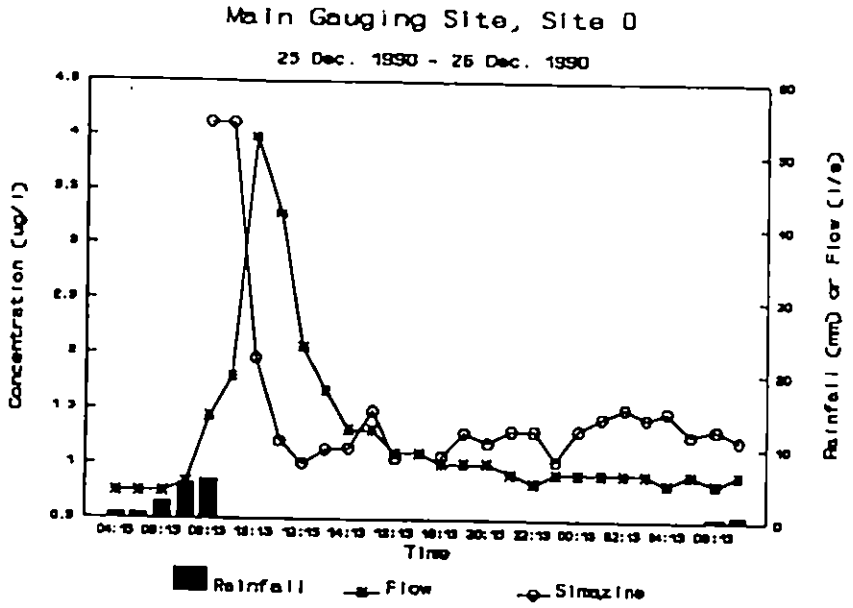

Figure 4.6 **Simazine concentrations leaving the Rosemaund catchment following a rainfall event after application.**

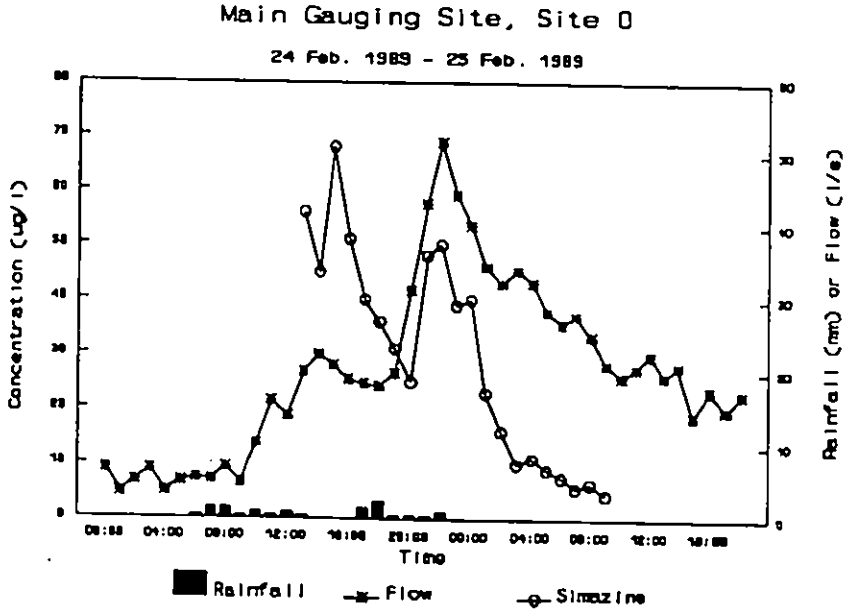

Figure 4.7 **Simazine concentrations in the stream leaving the Rosemaund catchment following rainfall after an application.**

with a pesticide flush albeit of slightly lesser magnitude each time.

The second explanation assumes an instantaneous equilibrium is reached between dissolved and solid phases, and that the shape of this type of event is a consequence of having a by-pass flow system present in the soil. In this model, soil water from near the surface, which has a high pesticide concentration, is transported rapidly by the incoming rainfall to the drains

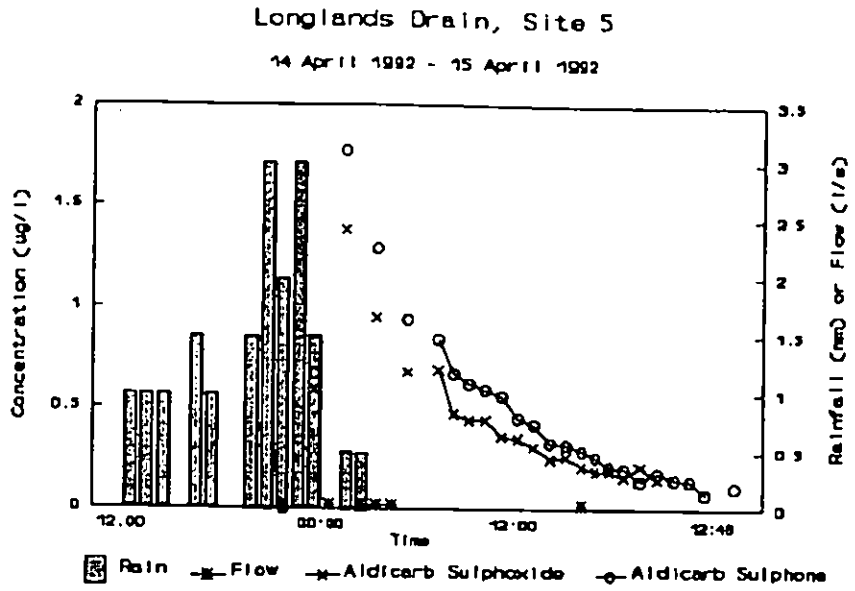

Figure 4.8 **Concentrations of the breakdown products of aldicarb in the drains under Longlands field following rainfall after an application.**

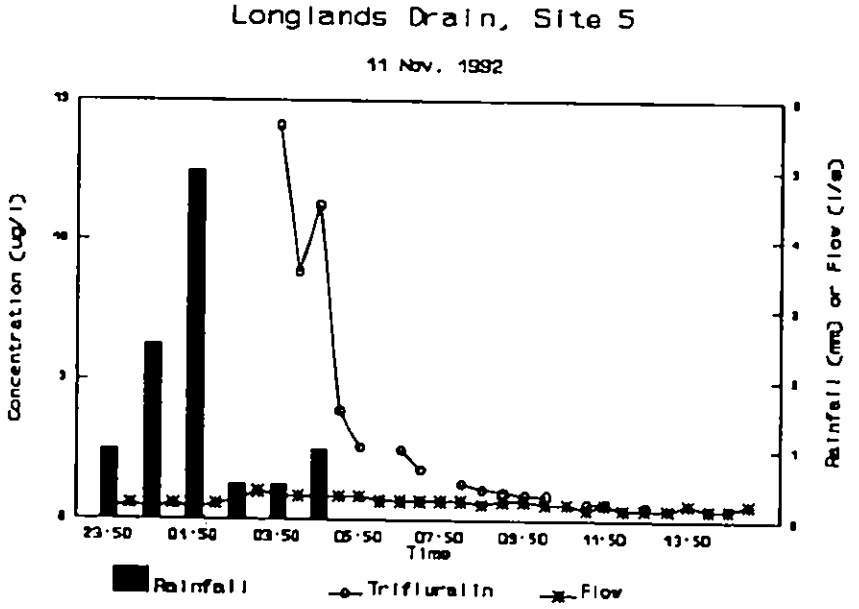

Figure 4.9 **Concentrations of trifluralin in the drains under Longlands field following rainfall after an application.**

via macro-pores. Since an instantaneous equilibrium is assumed this occurs throughout the rainfall event. Water is, however, moving via the larger pores in the soil matrix, especially in the highly conductive zone around the drains, and is much larger in volume than the macro-pore flow. The pressure exerted by this water will after some hours cause the water in the deeper layers (and of low pesticide concentration) to flow toward the drains and thus dilute the water from the macro-pores.

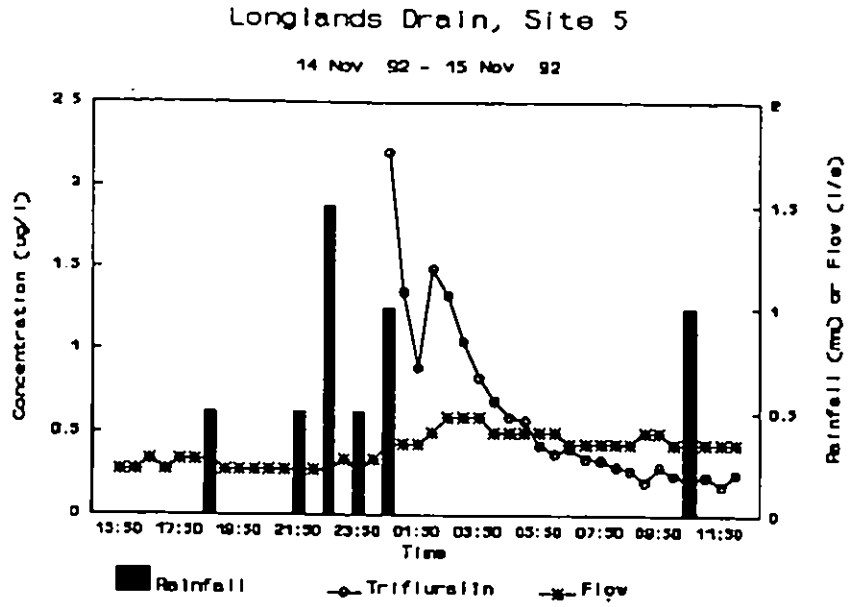

Figure 4.10 Concentrations of trifluralin in the drains under Longlands field following the second rainfall event after application.

In reality the explanation may be a combination of both of these hypotheses. They have in common the need to move water rapidly from the surface to the drainage system, which requires the presence of macro-pores. The generation of drain and stream flow is certainly not solely controlled by the movement of water from the surface and some contribution is made from the deeper soil water. Although there is some evidence that equilibrium may not be instantaneous under field conditions, such a combination leads to a very complicated conceptualization of the system and therefore, for the purposes of modelling Rosemaund, the second of the two hypotheses stated above has been adopted (see Section 5.2).

Type 3 Events

In this type of event, instead of rainfall causing a peak in pesticide concentration, a reduction in concentration is observed. This type of event has only been observed in on two occasions in late spring 1992 and is illustrated well in Figure 4.11. Isoproturon concentrations are shown for site 0 following a very intense rainfall event. The initial concentration was high (around 8 µg/l) but fell rapidly through the hydrograph to 1 µg/l. Levels then recovered to close to their original values by the end of the event. A similar response was observed at the same site during a smaller event which occurred some 10 days later (Fig. 4.12).

This type of response is typical of a contaminant that is being supplied to the stream by the base flow which is then diluted by clean water from incoming rainfall. Thus during the event the base flow concentration is first diluted by clean rain water moving rapidly from the top soil to the drains, but then rises again as the proportion of deeper soil water increases on the recession limb of the hydrograph.

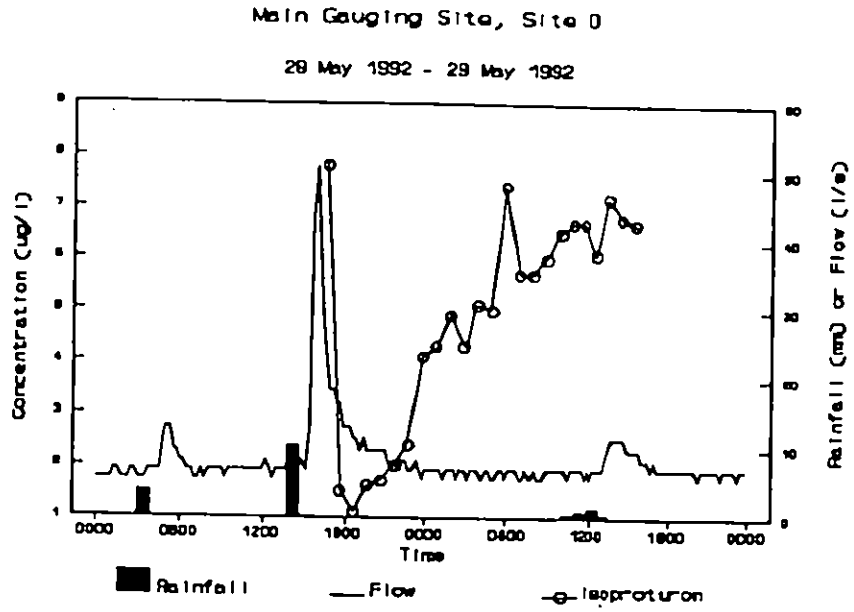

Figure 4.11 **Isoproturon concentration in the stream leaving the Rosemaund catchment following a rainfall event following an autumn application.**

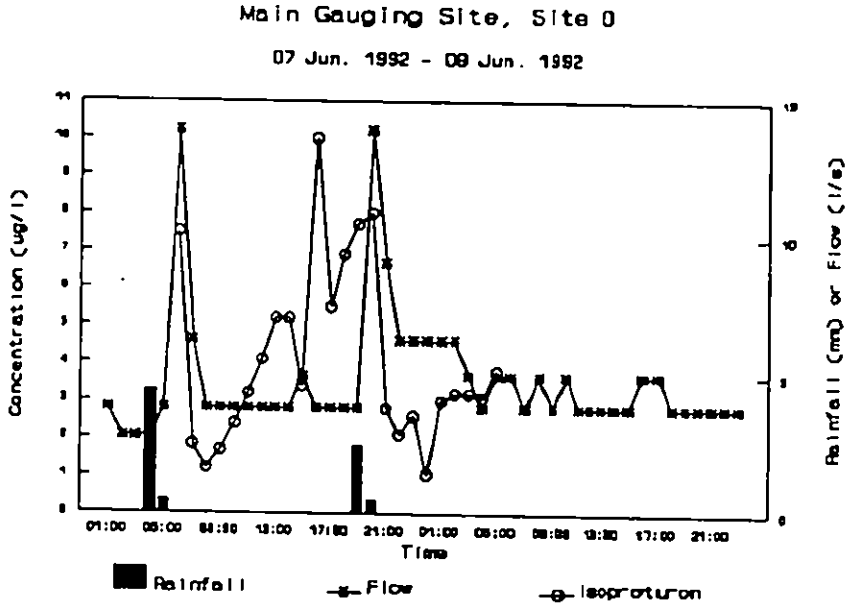

Figure 4.12 **Isoproturon concentrations in the stream leaving the Rosemaund catchment after rainfall following an autumn application.**

4.2.3 Particulate Pesticide Transport

The significance of particulate transport for the movement of pesticides to streams and drains was investigated in the final phase of the Rosemaund study through use of the highly sorbed chemical trifluralin (K_{oc} = 8000). Samples were taken from Longlands drain for three rainfall events following trifluralin application using the normal methods described in section 3.2. Three samples containing the highest sediment loads (by visual inspection this was the first

three samples in each case) were selected and sent to the Institute of Freshwater Ecology (IFE) River Laboratory, Wareham for separate analysis of the particulate and dissolved pesticide concentrations. The concentrations of pesticide in mobile bed sediment were also measured during and after a large event.

Table 4.4 gives details of the concentrations and mass loads carried in the water samples taken from Longlands drain. Both the highest concentrations of trifluralin and of sediment were found in the first event of 11 Nov. 1992. However, the highest of the three pesticide values for this event was from the first sample in which the vast majority (92% by weight) of the pesticide was transported in the dissolved phase. In the third sample in this first event the pesticide transported was divided equally between the particulate and dissolved phases. In only two events did the particulate load of pesticide exceed that in the water phase. The third event was only sampled at the tail of the hydrograph and consequently sediment loads were low as were the loads of associated pesticide.

As was noted in Section 4.2.2, above the highly sorbed nature of this pesticide does not seem to alter the way in which it responds to rainfall i.e. it fits well into the set of Type 2 events described above. Since this highly sorbed chemical seems to have behaved in the same manner as the less sorbed pesticides discussed earlier, then it maybe reasonable to treat it in the same way. Certainly the significance of particulate transport of the less sorbed chemicals that are commonly found in surface water can be considered negligible. This conclusion is based on a small data set for one chemical, sufficient resources were not available for a more extensive study of pesticides of this type.

Table 4.4 Details of trifluralin concentrations and suspended sediment loads in three rainfall events collected from Longlands Drain, Site 5

Date	Mass of Sediment (g)	Volume of Water (litres)	Trifluralin Concentrations			
			Suspended Sediment		Filtered Water	
			Concentration (µg/g)	Load (µg)	Concentration (µg/l)	Load (µg)
11 Nov 92	1.092	0.970	1.044	1.14	12.9	12.51
11 Nov 92	1.866	0.970	1.554	2.90	5.9	5.72
11 Nov 92	2.991	0.960	1.618	4.84	6.2	5.95
15 Nov 92	0.353	0.955	2.215	0.78	1.4	1.34
15 Nov 92	0.567	0.960	1.834	1.04	0.32	0.31
15 Nov 92	0.492	0.960	1.110	0.55	0.32	0.31
26 Nov 92	0.033	1.043	0.848	0.03	0.32	0.33
26 Nov 92	0.027	0.980	1.185	0.03	0.27	0.26
26 Nov 92	0.003	0.980	0.867	0.00	0.37	0.36

Mobile Sediments

The concentrations of trifluralin in mobile surface sediments in the stream during rainfall events are given in Table 4.5. The concentrations were quite similar in all the samples

collected and in all cases were much lower than the concentrations measured on the suspended particles. This limited data suggests that the fine particles are responsible for the bulk of the pesticide transport and these are not deposited on the stream bed during or after events. It is of interest whether these concentrations in the sediment are of any environmental concern.

Table 4.5 Trifluralin concentrations measured in the mobile bed sediments during rainfall events.

Date	Site	Concentration (µg/g)
24 Nov 92	0	0.020
25 Nov 92	1	0.140
25 Nov 92	1	0.079
30 Nov 92	1	0.053
30 Nov 92	1	0.074

Overland Flow

Trifluralin concentrations were also measured in water samples collected by the overland flow traps following a number of rainfall events, these results are given in Table 4.6. It should be noted that the design of the traps removed large particles before the water sample was collected; fine particles could remain in the collected water. The highest concentrations were measured following the first rainfall event after application. Thereafter runoff concentrations were about an order of magnitude lower for all traps. The concentrations measured in the traps were quite similar and imply an even application of pesticide to the field. It is clear that rainfall events occurring soon after rainfall have the maximum likelihood of producing high pesticide concentrations in overland flowing water.

Table 4.6 Trifluralin concentrations measured in surface runoff traps in Longlands field following rainfall events.

Date	Trifluralin Concentrations (µg/l)			
	Trap 1	Trap 2	Trap 3	Trap 4
12 Nov 92	20.0	86.0	15.5	-
09 Dec 92	2.5	0.15	0.43	1.74
27 Dec 92	0.99	0.91	2.0	0.61
20 Jan 93	0.80	1.55	-	-

4.2.4 Pesticide Runoff and Physico-chemical properties

It was observed in Section 4.2.1 above that there was an apparent relationship between the physico-chemical characteristics of a pesticide and its detection during monitoring at Rosemaund. This section proposes an index of pesticide runoff, I_m which is based on the relationship between three factors that might logically influence peak concentrations. These three factors are:

1. The half life of the pesticide assuming a first order decay reaction,
2. The length of time between the pesticide application and the rainfall event,
3. The area of the catchment above the sampling site.

The factors are combined thus;

$$I_m = (M*e^{-kT})/A$$

where M is the mass of pesticide applied (kg), k is the decay rate of the pesticide ($days^{-1}$), T is the time between application and rainfall event (days), and A is the area of the catchment above the sampling site. If there has been more than one application then the effective I_m is the sum of the individual indexes for each application. The logic behind this choice of index is that the time between application and rainfall event combined with the pesticide half life gives an estimate of the amount of pesticide left in the catchment. The catchment area is used as a surrogate for flowrate i.e. larger catchments generate larger flows. If the area treated is small compared to the catchment area then the value of I_m will be small.

Values of I_m have been calculated for all the events monitored at Rosemaund and the values are presented in Table 4.1. Figure 4.13 presents the same data graphically by plotting the peak pesticide concentration against the index, I_m. The plot identifies each sampling site by representing each point by the site number to which it refers. A cluster of values can be seen close to the origin showing that many events had a low peak concentration and a low value of I_m. In general the expected trend of increasing value of the index and increasing peak concentration is followed. However, the correlation is too poor to formulate a usable mathematical relationship. There is a clear grouping of the points into sites with site 0 having the lowest values of I_m and site 5 the highest. This is due to the inclusion of the catchment area in the formulation of the index and the fact that higher proportions of individual fields get treated than the catchment as a whole. An alternative plot of flow weighted mean concentration against I_m is shown in Figure 4.14. As would be expected a similar pattern is observed with the separation by site still apparent.

Although the value of I_m cannot be used to estimate the peak pesticide value directly it is possible to define a threshold value that can be used to predict when a given maximum concentration will not be exceeded. For example, using the data in Table 4.1, a value of I_m of less than 0.005 kg/ha will give a maximum pesticide concentration of less than 0.22 µg/l and less than 0.1 µg/l in the vast majority of cases.

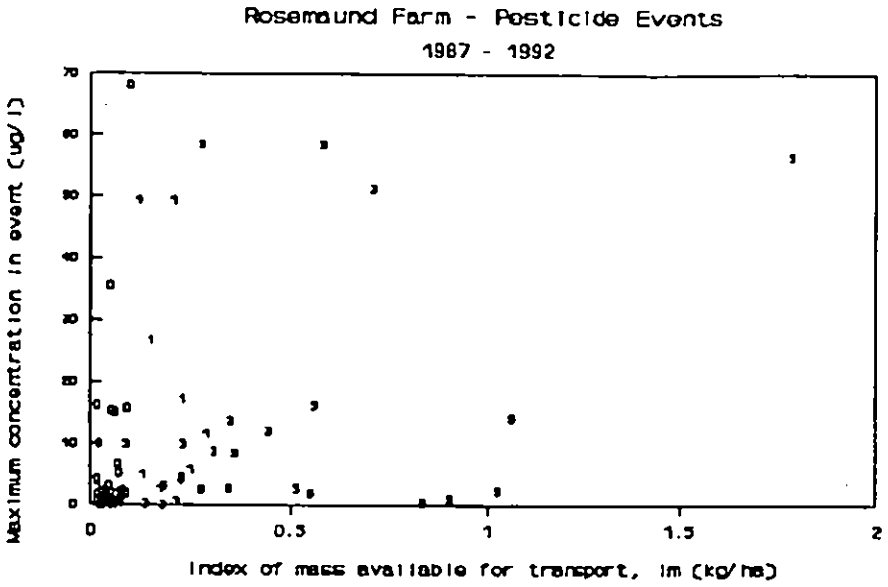

Figure 4.13 **Index of available mass against maximum pesticide concentration. Numbers indicate the monitoring site where the data were collected. Peak value of 264 µg/l not shown to aid clarity of the graph.**

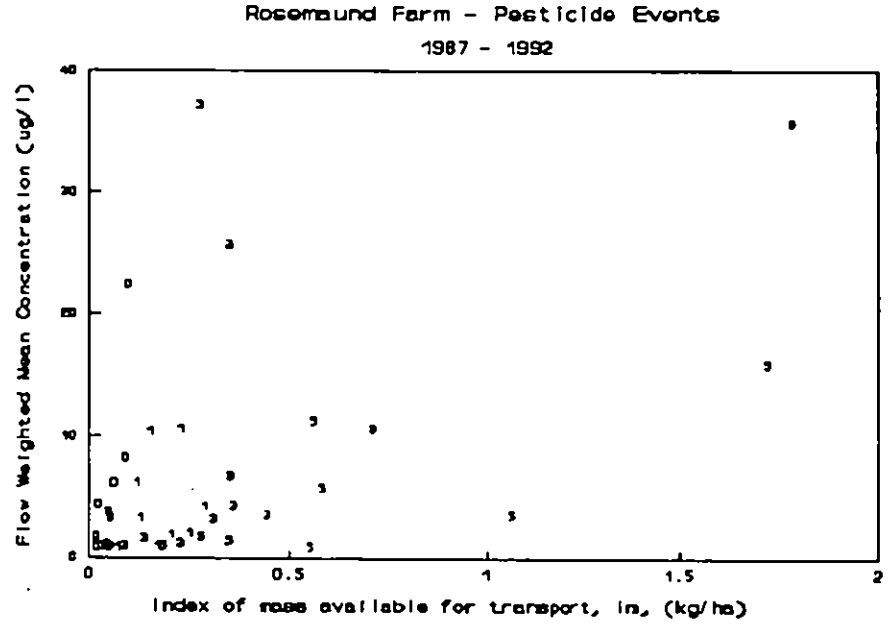

Figure 4.14 **Index of available mass against flow weighted mean concentration. Numbers indicate sampling site from where data were collected.**

Any relationship developed between an index such as I_m and observed data is clearly only empirical even if it is based on common sense relationships. Empirical relationships are only valid within the bounds of the data from which they have been derived and can not be used safely on more general problems. The lack of a good correlation between I_m and either peak or mean pesticide concentrations indicates that the problem of pesticide runoff is more

complicated than considered in this treatment. There is therefore a need for a more sophisticated approach such as that outlined Section 5. below.

4.3 *Gammarus Pulex* Bioassay

In general the bioassays revealed little stress to the target animals, as measured by their feeding rate, to pesticide exposure. However, on one occasion, all the animals were found to be dead following a large rainfall event which transported high concentrations of carbofuran to the stream (Mattheissen *et al.*, 1993). The event occurred 36 days after the carbofuran application and gave rise to an initial peak concentration of 24 µg/l, 10 hours after the start of the rainfall. A second, higher peak, of 27 µg/l occurred 15 hours after the first after which concentrations declined to 1.9 µg/l after 4 days. The rainfall event was of an unusual intensity (71.5 mm in 25 hours) and has a return period of 50 years. The mean dissolved oxygen levels during the field experiments ranged from 48 to 59 % saturation, and mean pH values between 7.4 an 7.9, both well within the acceptable range for *Gammarus* species. Laboratory experiments were conducted under similar conditions to check whether carbofuran was toxic to *Gammarus* at these concentrations. The experiments showed that carbofuran to be very toxic with 24, 48 and 96 hour LC50 values (concentration at which 50% of the population dies in a given time) of 21.0, 12.5 and 9.0 µg/l respectively (Matthiessen *et al.*, 1993). It is therefore likely that at least a proportion of the deaths observed at site 1 were due to elevated concentrations of carbofuran.

5. PESTICIDE MODELLING

5.1 Background

One of the main objectives of the Rosemaund study was to collect field data on the movement of pesticides to surface waters for the development and testing of mathematical models. Prior to this study, the majority of data collection studies and modelling work had been conducted in the United States of America where models of pesticide movement were of one of two types; those which considered only vertical movement of water and solute to groundwater and those that estimated surface runoff concentrations at the edge of treated fields. In the former category examples are the Pesticide Root Zone Model (PRZM, Carsel *et al*, 1984) and the Leaching Estimation and Chemistry Model, Pesticides (LEACHP, Waganet and Hudson, 1989). In the second category can be found the Agricultural Runoff Management (ARM) model (Donigan *et al*, 1977), Chemical, Runoff and Erosion from Agricultural Management Systems (CREAMS) model (Knisel, 1982) and the Pesticide Runoff (PESTRUN) model, (Mcall and Lane, 1982). It is clearly this second set of models that is of most interest to this study and a brief summary is given below of each of these models.

5.1.1 PESTRUN

This model is based on a mass balance of the top 1 cm of soil and is a modification of an earlier model (Haith, 1980). Any water percolating below 1 cm is considered not to be available for runoff. The pesticide is distributed uniformly through the top 1 cm and distributed between the soil and the soil water according to a single valued linear equilibrium isotherm. The total loss of pesticide in a rain event is taken as the sum of pesticide sorbed onto eroded soil and pesticide in runoff water. Soil loss is estimated through the Universal Soil Loss Equation (Williams, 1975), and runoff is estimated using the Soil Conservation Service Number Equation (Mokus, 1972). Both of these methods are empirical and based on parameters available from soil surveys of US soils. Degradation of pesticide is assumed to be described by a first order decay rate and acts to reduce the pesticide pool between rainfall events. This particular approach is not applicable to Rosemaund where percolation to subsurface drainage is a significant pathway for pesticide runoff.

5.1.2 ARM

The ARM model takes a more holistic approach to the soil environment than PESTRUN. The soil is divide into four zones, the surface zone, upper zone, lower zone and groundwater zone. Soil water, pesticide and sediment sub-models act on these zones and the sum of the outputs from the zones makes up the total transport from the system. The hydrological model is based on the Stanford Watershed Model (Crawford and Lindsay, 1966). This model simulates the response of a catchment to evaporation and rainfall inputs by a moisture accounting procedure for each component of the hydrological cycle. Sediment is modelled as detachment followed by transportation. Detachment is a power function of rainfall and is output to a storage reservoir, subsequent transport is based on a power function of flow. The characteristics of the sediment are considered to be the same as the parent soil. Transport of pesticide from the catchment is via a combination of soil erosion and water movement. Pesticide is distributed

between the solid and dissolved phase according to a single value adsorption isotherm and first order degradation takes place in both these phases.

5.1.3 CREAMS

This model is designed for field sized areas, is physically based and does not require calibration. Input data requirements have been restricted to those that are readily available or easily measurable. It is a model for evaluating responses from a range of agricultural management practices and is not a predictive model. It provides estimates of relative responses to given scenarios and should only be used for evaluating a range of agricultural management practices.

CREAMS (Knisel, 1982) has three major components; hydrology, erosion and chemistry. Each operates separately and generates information to be used in the other components. The hydrology component estimates the water balance elements with options for calculating direct runoff. One option requires daily rainfall, the other requires hourly or intensity data and uses an infiltration equation to partition rainfall into infiltration and direct runoff. The hydrology component calculates storm runoff volume, peak rate, storm rainfall energy, percolation and soil water accretions for each storm event. Between events, evaporation, transpiration percolation and soil water content are calculated.

The erosion component calculates rill and inter-rill erosion, transport and deposition for any shape of overland flow profile. Sediment transport from overland flow is input to the concentrated flow area or channel. Sediment yield at the field edge and sediment enrichment ratios, based on particle size distributions are calculated for use in the chemical component. The chemistry component calculates water and sediment fractions of pesticide load for the field.

The model has been modified to include the vertical flux of pesticides in addition to the surface runoff processes describe above. This model is known as GLEAMS, Ground water loading effects of Agricultural Systems, (Leonard, 1987). This is one of the few models that considers both vertical and lateral movement of pesticides in some detail.

5.1.4 Application in the UK

Of the models described above perhaps of most interest is the CREAMS model. Its claim of requiring no calibration and its detailed consideration of surface runoff is certainly attractive. However the parameter base for the model is heavily dependent on the databases produced by the US Soil Conservation Service for US soils. Such data probably do not exist in the required forms at present for UK soils, although work has recently been started on the collation of such data for UK soils for use in solute modelling by the SSLRC. CREAMS at present does not take account of runoff on structured clay soils which may have sub-surface drainage, an important class of soils in UK agriculture; although again recent work is moving in that direction. For these reasons it was considered desirable to adopt a new approach to pesticide modelling which has been an objective of this study.

In the UK the most 'at risk' time for surface waters from pesticide runoff is in the autumn and early spring when soil moisture deficits are low. At these times of year the crops cover a small part of the field area and the rooting systems are shallow. There is therefore scope for a simple model that ignores the influence of the crop and considers only the period of soil drainage. At the same time the model should take account of the important processes controlling pesticide transport (eg pesticide physico-chemical properties) and the influence of water pathways. The implementation of this approach within the framework of a lumped modelling approach should reduce the data input requirements while retaining a mechanistic approach. A model based on compartments, determined by water flow paths, in which chemical reactions are allowed to proceed, allows for inclusion of simple representations of by-pass routes and drainage systems. These are the fundamental ideas that have led to the modelling approach adopted for Rosemaund.

5.2 Rosemaund Model

5.2.1 Introduction

One of the objectives of the IH/NRA Authority part of the Rosemaund Study was to develop a simple model of pesticide runoff from catchments which could be used to help the NRA develop sampling strategies for pesticides within surface waters based on some knowledge of pesticide use. Clearly this end objective is very ambitious and the work to date has been directed at developing a model that will simulate pesticide concentrations arising from Rosemaund Farm.

The soils at Rosemaund are predominantly clay/loam in texture and from the Bromyard series. These soils are prone to seasonal water logging and consequently nearly all the fields at Rosemaund are drained, (typically 1 m depth, 20 m spacing). During the summer the soils can crack and these cracks may persist at depth through part or all of the drainage period. There are also macro-pores extending to depth and spaces around soil peds in the lower parts of the profile. It is obvious therefore that the route water takes to the drains and the stream will influence the pesticide content of the water and that any mechanistic model must attempt to describe these different water pathways.

5.2.2 Model Structure

The model structure presented here is derived from detailed measurements of the soil water movement and distribution in Longlands field over successive winters by members of the Agrohydrology section of the Institute of Hydrology (see Section 4.4 and Bell *et al*, 1991 and 1992). Broadly, an underdrained field at Rosemaund Farm consists of two types of soil profile which are characterised by the rate at which they allow downward water movement. The bulk of the soil in the inter-drain position has a very low hydraulic conductivity which approaches zero when the soil is saturated; downward water movement through the soil matrix is therefore very slow. The soil above the drains seems to have a much higher hydraulic conductivity and thus water movement through the soil matrix in this part of a field is much quicker. Thus, once the soil below the drains is saturated and the drains begin to flow the

hydrological response of the drain is controlled by the soil immediately above and adjacent to the drains.

A diagrammatic representation of the model is shown in figure 5.1. The model considers the top 2 m of the soil profile which is divided into three layers above the level of the drains and one below. Above the drain the layers are subdivided into two to represent the fast and slow parts of the soil profile described above. The fields are generally sloping and in this conceptualization the drain zone is considered to be down slope of the inter-drain zone. The consequent possible directions of water movement are shown by the arrows in figure 5.1., where dotted arrows indicate the possibility of water moving directly to lower layers (via macropores and/or cracks) without interacting with intervening layers. The transport of pesticide in the system is assumed to be associated with the water movement, the pesticide being partitioned between the soil and water phases at the end of each time-step. The model keeps account of the amounts of water and the dissolved and absorbed pesticide in each box and calculates changes to these depending on a mass balance of inputs, outputs and internal sources and sinks.

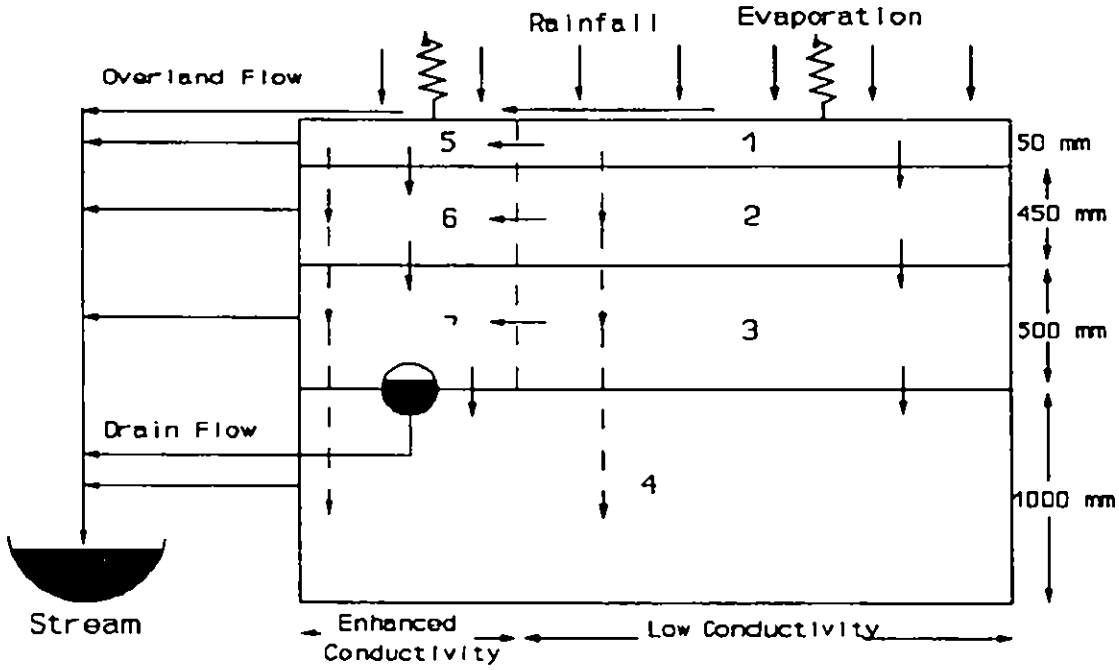

Figure 5.1 Rosemaund conceptual pesticide model showing division into compartments and water pathways.

Water Movement

To explain the details of water and pesticide movement it is best to consider a single box from the model (Fig 5.2).

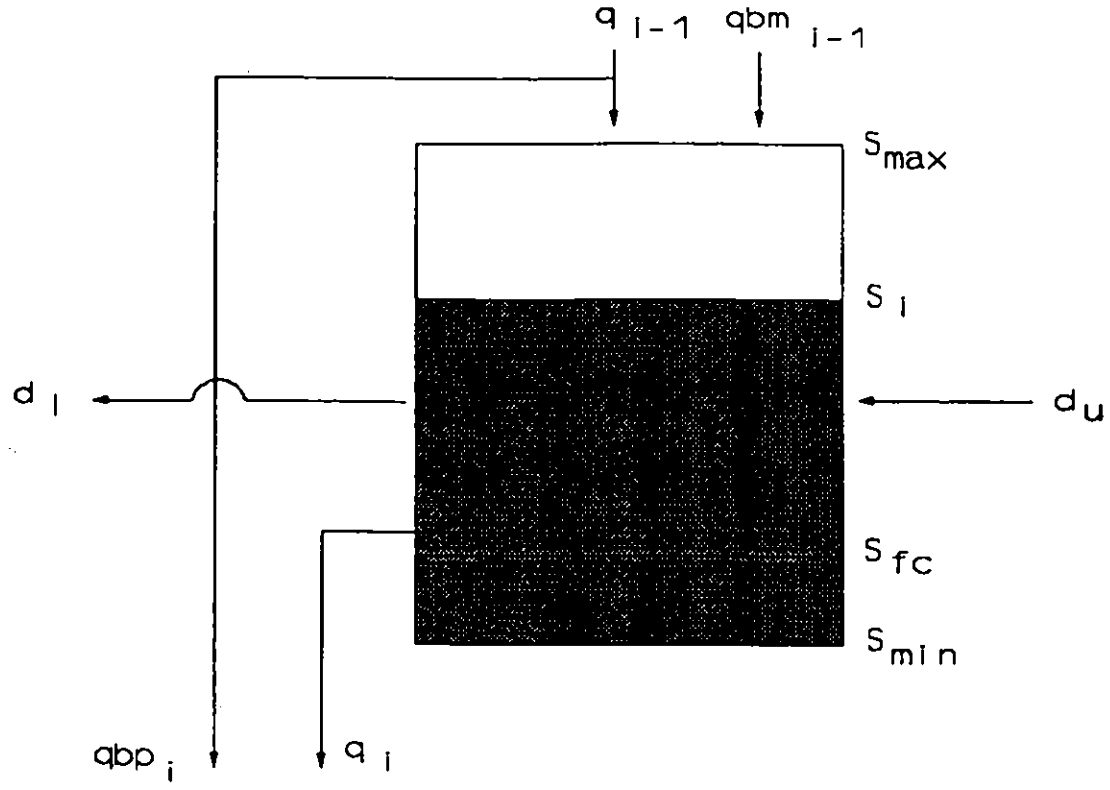

Figure 5.2 Main water pathways through a single box taken from the Rosemaund pesticide model.

Let the subscript i, be used to refer to one of the seven boxes in figure 5.1 above. The change in soil water content of box i, S_i is given by;

$$\frac{dS_i}{dt} = q_{i-1} - qbp_i + d_u - q_i - d_l + qbm_{i-1}$$

where q_i is the flow per unit (mm) area from box i; d_u is the flow per unit area (mm) from an up-slope box, d_l is the flow to a down-slope box or stream; qbp_i is the flow from box i-1 that by-passes box i in cracks or macro-pores; qbm_{i-1} is the flow that was in by-pass routes in box i-1 that return to the soil matrix in box i; t is time (hours). Flow may only occur from box i , either vertically (q_i) or laterally (d_l) when $S_i > SFC_i$, where SFC_i is the field capacity of box i. Flow from box i depends on the water content of box 1 and is given by;

$$q_i = k_v(S_i - SFC_i)(1-\tan(\alpha))$$

where k_v (hours^{-1}) is a measure of the vertical conductivity of box i, and α is the average slope of the field. Similarly the down slope drainage d_l is given by;

$$d_l = k_s(S_i - SFC_i)\tan(\alpha)$$

where k_s is a measure of the horizontal conductivity of box i. A fraction of water may by-pass a given layer through macro-pores and cracks. The fraction of by-pass flow through a box is related to the soil water content of the box, such that the drier the box the more by-pass flow can occur. This feature of the model is to take some account of the swelling nature of the soil. The by-pass flow fraction CF_i is given by;

$$CF_i = CFMIN_i + G_i(S_i - SMIN_i)$$

where

$$G_i = (CFMIN_i - CFMAX_i)/(SMAX_i - SMIN_i)$$

where $CFMIN_i$ is the minimum bypass flow fraction occurring at maximum water content, $SMAX_i$ and $CFMAX_i$ is the maximum bypass flow fraction occurring at minimum soil water content $SMIN_i$. Therefore,

$$qbp_i = CF_i q_{i-1}$$

The continuity of cracks through layers is given by the ratio, CF_i/CF_{i-1} to a maximum of unity. Thus, once in a crack, water is assumed to remain there until the crack ends, hence,

$$qbm_i = \left(1 - \frac{CF_i}{CF_{i-1}}\right) qbp_{i-1}.$$

Water may only enter a box if it is not saturated (ie $S_i < SMAX_i$), $SMAX_i$ is given by;

$$SMAX_i = \theta_i V_i$$

where θ_i and V_i are respectively the porosity and volume (mm) of box i.

Pesticide Movement

Pesticide is added to the model by assuming that the amount applied is well mixed into the top layer of the model (boxes 1 and 5, Fig 5.1) and partioned following a reversible instantaneous linear sorption isotherm,

$$PS_i = PW_i kd_i$$

and

$$kd_i = k_{oc} OC_i$$

where PS_i is the pesticide concentration in the soil phase, PW_i is the concentration of the dissolved phase, kd_i is the partition coefficient, k_{oc} is the partition coefficient normalised for organic carbon content, OC_i.

The rate of change of mass of dissolved pesticide in the ith box, (S_iPW_i) is given by,

$$\frac{dS_iPW_i}{dt} = (q_{i-1} - qbp_i)PW_{i-1} + d_uPW_u - (q_i + d_i)PW_i + qbm_{i-1}PW_{bm} - R_dPW_i$$

where, PW_i is the dissolved pesticide concentration per unit area of the ith box (µg/mm), PW_u is the pesticide concentration of water draining from an up-slope box, PW_{bm} is the concentration of pesticide in the bypass flow and R_d is the first order rate coefficient describing degradation of the pesticide. Water moving through by-pass routes is assumed to have the same concentration as the soil water in the box with which it was last in contact. The rate of change of mass of pesticide absorbed onto the soil is given by;

$$\frac{dPS_i}{dt} = - R_dPS_i$$

where, PS_i is the soil absorbed pesticide concentration per unit area in the ith box (µg/kg/mm^2). The degradation rate of the pesticide is assumed to be the same in both the liquid and solid phase. At the end of each model time step (one hour) the pesticide is repartitioned between the soil and the soil water using the linear isotherm described above.

Drainflow

The model only allows drainflow when the deep soil box, (box 4, Fig 5.1) is at saturation. When this occurs, drainflow is the sum of the vertically draining water from boxes 3 and 7 plus any water from rainfall and boxes 5 and 6 moving via by-pass routes. Water moving from boxes 3 and 7 is assumed to produce drainflow by displacement of water from box 4, while water in bypass routes is directly intercepted by the drain. The concentration of pesticide in the drainflow is thus a mass balance of the contributions from the various flow paths.

Stream Flow

Stream flow is the sum of the lateral drainage from each of the boxes, and drain flow. Again the concentration of pesticide is a mass balance of the contributions from all the flow paths. Overland flow is generated when rainfall less evaporation and drainage exceeds the capacity of box 1 to contain water. Water flowing overland from box 1 will infiltrate into box 5 if this box is not saturated. The concentration of pesticide in the overland flow is assumed to be equal to the concentration of the box from which it was generated.

5.2.3 Model Application

The model has been used to simulate the pesticides isoproturon, lindane, simazine, mecoprop, trifluralin and dichlorprop in both field drains and at two locations in the stream.The model is driven by hourly rainfall taken from the automatic weather station (AWS), (Fig 3.1). The AWS also provides estimates of potential penman evaporation which have been taken as

actual evaporations where the water content of the surface boxes is sufficient to meet the demand. The values of moisture volume fraction corresponding to SMIN, SMAX and SFC used in the model simulation are given in Table 5.1. The values of SMIN and SMAX, are based on PF curves generated for Longlands field by staff of the Agrohydrology section of the Institute of Hydrology. The values of SFC are best guess estimates.

Table 5.1 Values of the moisture volume fraction equivalent to minimum water content (SMIN), field capacity (SFC) and saturation (SMAX), used in the model.

Box No.	SMIN	SFC	SMAX
1 and 5	0.19	0.27	0.42
2 and 6	0.24	0.32	0.40
3 and 7	0.30	0.35	0.38
4	0.24	0.25	0.26

The organic carbon content and bulk density of the soil in each of the model boxes was estimated from analysis of soil profiles carried out by the Soil Survey and Land Research Centre. These values are given in Table 5.2.

Table 5.2 Organic carbon contents and bulk densities allocated to the boxes used in the model.

Box No.	Bulk Density (g/cm^3)	%Organic Carbon
1 and 5	1.21	1.7
2 and 6	1.42	0.9
3 and 7	1.38	0.5
4	1.38	0.5

Calibration of the model to Rosemaund involved the selection of the parameters controlling the movement of water between the boxes that represented the different hydrological compartments i.e the conductivities. The selection was guided by knowledge of the relative magnitude of the water flows estimated through the study of the soil water hydrology. Model predictions of flowrate from longlands field were compared to measured values for the events of January, February and March of 1991. All other simulations for different years and the additional monitoring sites were carried out using these parameter values.

In order to apply the model to different pesticides under the same hydrological conditions three parameters need to be changed; the amount and timing of pesticide applications, the partition coefficient normalized for organic carbon content, k_{oc}, and the degradation rate (half life). The pesticide application data were supplied by ADAS Rosemaund and the values of k_{oc} and degradation rate were obtained from the literature. The values of the k_{oc} and degradation rate used in the simulations are given in Table 5.3. No changes in degradation rate are currently made as a result of temperature, soil moisture content or depth.

Table 5.3 Physico-chemical parameters used in the pesticide model

Chemical	k_{oc} (ml/g)	Half life (days)
Isoproturon	130[3]	20[2]
Lindane	1100[1]	400[1]
Simazine	130[1]	60[1]
Mecoprop	20[1]	21[1]
Dichlorprop	1000[1]	10[1]
Trifluralin	8000[1]	60[1]

Source: 1 Wauchope *et al.*,1992
2 Fitted from Rosemaund data
3 D N Brooke *pers comm.*

Results and Discussion

The results of the model simulations are summarized in Table 5.4 for each event and pesticide combination. Comparisons are made between observed and modelled data in terms of the peak and flow weighted mean pesticide concentrations. The error in the prediction of the timing of the peak is also reported.

The model produced good estimations of the values of both the peak and flow weighted mean pesticide concentrations, generally to better than one order of magnitude. However the time for the peak concentration was not predicted well, the model always anticipating the observed peak by several hours. The identification of the peak value in the time series of concentrations representing an individual event can present difficulties given the different pesticide runoff patterns that have been observed. In figure 5.3 the observed and modelled data show a similar pattern but the curves are shifted in time; here it is easy to compare peak values and estimate a time error. In figure 5.4, on the other hand, the comparison is more difficult, the observed data having two peaks the second being higher than the first. Thus comparison of the peak modelled and observed concentrations in such situations gives a large error in timing. A third pattern of behaviour is shown in figure 5.5, where good correspondence was achieved between observed and modelled simazine concentrations for the event. However, the model suggests that, if sampling had started earlier, higher concentrations of simazine would have been found.

Table 5.4 Summary of the results of the simulation of pesticide concentrations at ADAS Rosemaund during a number of rainfall events.

Pesticide	Date of Event	Site No.	Obs. Mean[1] (µg/l)	Predicted Mean[1] (µg/l)	Error[4]	Obs. Max. (µg/l)	Predicted Max. (µg/l)	Error[4]	Time Error (hours)
Isoproturon	8/11/89	3	4.3	1.4	-0.49	8.4	15.0	0.25	10
	10/11/89	3	6.7	1.2	-0.75	13.7	8.0	-0.24	5
	13/12/89	3	3.2	0.93	-0.54	8.8	12.6	0.16	8
	13/12/89	1	3.3	3.9	0.07	5.4	13.9	0.41	12
	25/12/90	0	0.49	2.4	0.70	1.8	6.8	0.58	13
	25/12/90	1	10.6	4.2	-0.40	17.2	12.3	-0.14	2
	5/01/91	0	0.36	1.6	0.64	5.2	2.5	-0.32	20
	8/01/91	0	0.60	1.4	0.37	6.7	1.7	-0.60	20
	8/01/91	1	0.96	2.5	0.42	2.6	3.1	0.08	3
	8/01/91	5	0.14	2.7	1.30	0.40	5.9	1.17	7
	21/02/91	0	<0.02	0.24	>1.10	<0.02	0.30	>1.18	-
	21/02/91	1	0.92	0.43	-0.33	2.1	0.50	-0.62	2
	21/02/91	5	1.4	0.73	-0.28	2.6	1.2	-0.34	6
	4/03/91	5	1.7	0.53	-0.51	2.3	0.80	-0.46	24
Lindane	8/11/89	3	1.2	0.35	-0.54	4.6	3.5	-0.12	6
	8/11/89	5	[2]0.85	0.90	0.02	1.9	8.8	0.67	10
	10/11/89	3	1.2	0.35	-0.54	4.1	2.7	-0.18	5
	13/12/89	1	0.12	0.67	0.74	0.30	2.4	0.90	10
	13/12/89	3	0.14	0.27	0.28	0.50	2.9	0.76	7
	16/12/89	0	[2]0.16	0.17	0.02	0.40	0.50	0.10	-[3]
	16/12/89	5	[2]0.57	0.64	0.05	2.5	4.6	0.26	-[3]
Simazine	24/02/89	0	22.4	32	0.15	68.0	101.0	0.17	5
	2/03/89	0	8.2	28	0.53	13.9	87.6	0.80	8
	24/02/89	1	0.50	4.4	0.96	12.8	1.8	0.85	12
	25/12/90	0	1.7	0.41	-0.62	4.1	1.4	-0.47	1
	5/01/91	0	0.90	0.35	-0.41	1.5	0.60	-0.40	8
	8/01/91	0	[2]0.5	0.33	-0.20	0.70	0.40	-0.24	1
	21/2/91	0	0.26	0.17	-0.18	0.40	0.20	-0.30	5
	16/03/91	0	3.3	7.8	0.38	15.3	26.2	0.23	3
Mecoprop	15/5/90	1	0.30	0.78	0.42	1.4	5.2	0.57	16
Dichlorprop	15/5/90	1	0.35	0.23	-0.18	1.0	1.5	0.18	14
Trifluralin	11/11/90	5	3.7	0.64	0.76	14.1	14.9	0.03	2
	15/11/90	5	0.39	0.12	0.51	2.2	1.2	-0.26	1

Notes:
1 Flow weighted mean.
2 Simple mean (no flow data available).
3 More than one rainfall event during sampling period.
4 LOG_{10} (Predicted/observed), 0 is perfect fit, >1 or <-1 fit worse than order of magnitude.

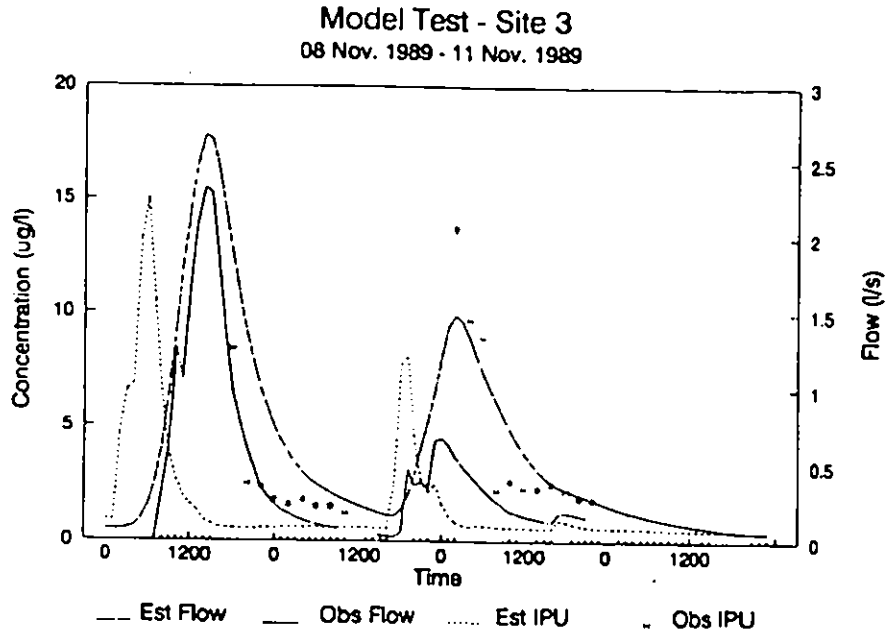

Figure 5.3 **Flow rate and isoproturon concentrations estimated using the Rosemaund model compared with observed values for site 3.**

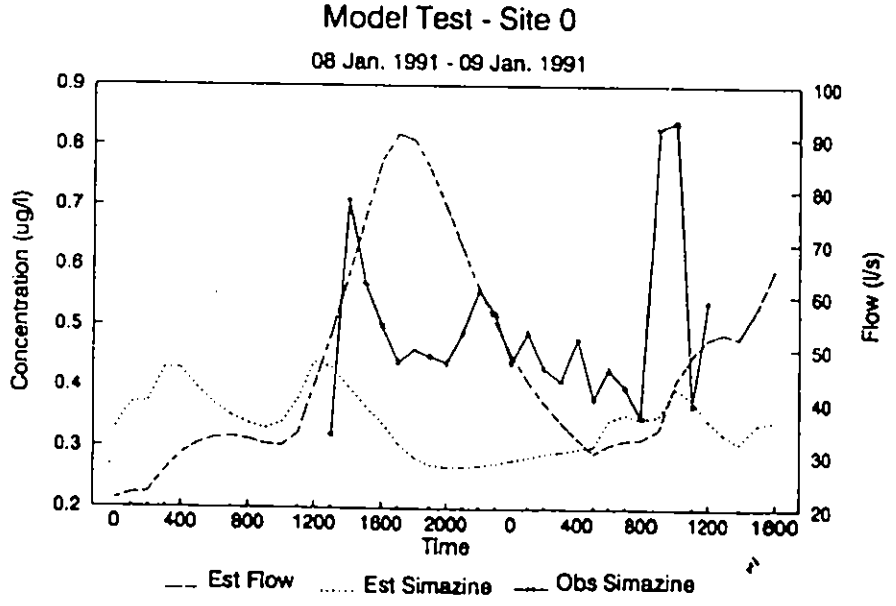

Figure 5.4 **Flow rate and simazine concentrations estimated using the Rosemaund model compared to observed values for site 0.**

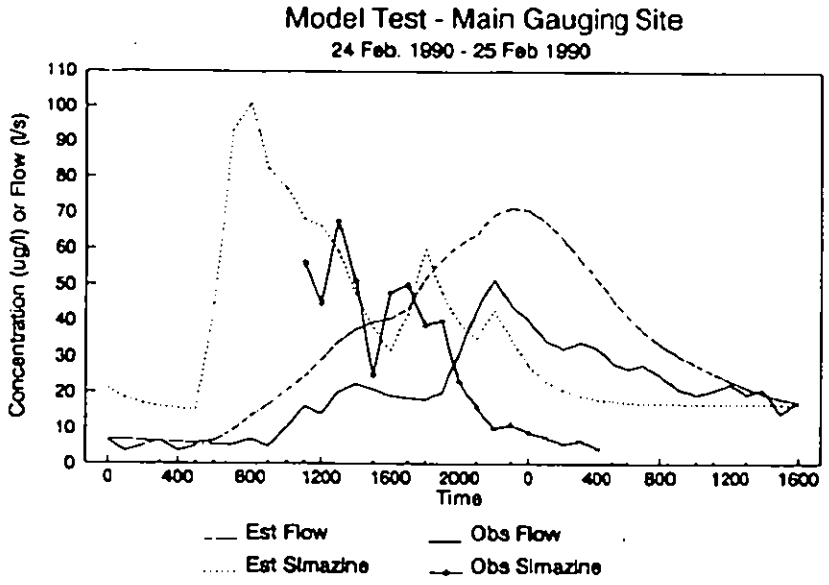

Figure 5.5 **Flow rate and simazine concentrations estimated using the Rosemaund model compared with observed values for site 0.**

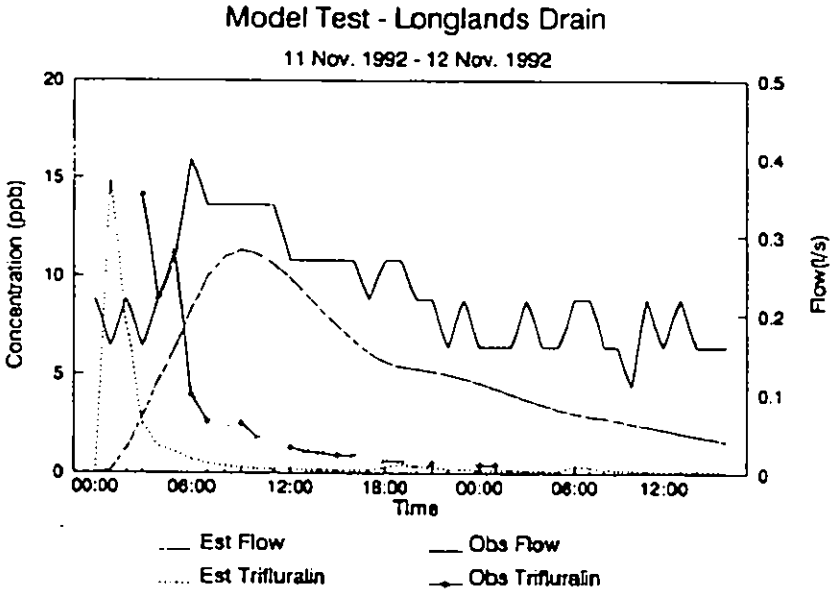

Figure 5.6 **Flow rate and trifluralin concentrations estimated using the Rosemaund model for site 5.**

Of particular interest is the fact that the model predicted concentrations of trifluralin as effectively as for any of the other chemicals that were simulated. This confirms the assumption made by the model that even fairly highly sorbed chemicals can be treated in a similar fashion to more soluble chemicals (Fig. 5.6).

5.2.4 Model assumptions and limitations

All models are based on a number of assumptions which will have a bearing on the circumstances in which the model can be applied. This section lists the Rosemaund model assumptions and identifies how this might influence its application.

1) The model has been developed using data from ADAS Rosemaund and has been tested against observed data from this catchment. Considerable thought needs to be exercised before application to other catchments is attempted.

2) The system can be modelled as a series of linked well mixed compartments. Use of the model to predict the depth of percolation of pesticide through the soil profile is not recommended.

3) The model is a lumped model i.e. parameters are given a single value to represent an entire compartment. There is no spatial variability in the rate of movement of water and pesticide to the catchment outlet. Thus the size of catchment that can be modelled using this approach is limited.

4) An extensive proportion of the catchment is drained.

5) A cracking soil with macro-pores.

6) Instantaneous and reversible sorption of the pesticide.

7) The microbial degradation of the pesticide follows a first order decay reaction.

8) Degradation is independent of temperature and water content.

9) Little crop cover and is thus only valid under winter/early spring conditions when the soil profile is draining.

10) The hydrological year starts on 1 September, and that soil water stores are at their minimum at this time.

Of all the model limitations outlined above, the first three are the most important; 2) and 3) are basic assumptions in the conceptualization of the model and 1) emphasises the limited testing to which the model has been subjected. The conceptualization can be considered to be independent of location and will not affect the general applicability of the model, other than in the size of catchment that can be modelled as a single entity. There is insufficient

experience in applying the model to give a definitive maximum catchment size, however, a value of 1000 ha would be a good initial estimate.

Assumptions 6, 7 and 8 are commonly used in pesticide modelling and reflect the general availability of data to describe these processes. Assumption 9 means that the model should only be applied from winter to spring. However, this time frame covers the hydrological conditions most likely to lead to pesticide runoff and should not prove to be a limitation. The starting date for the model is fixed assuming that 1 September is the start of the hydrological year; in most years (and most locations within the UK) this assumption will hold.

Only assumptions 4 and 5 make specific demands on the soil type and drainage within a catchment on which the model is to be run. The model contains parameters that may be used to alter the macro-porosity of the soil and the extent of the drainage network so as to minimise the limitations of these assumptions. However, if the fraction of the catchment drained and the macro-porosity were to be set to zero, then care should be taken to ensure that the model produces sensible results. One approach would be to compare the hydrographs produced by the model with observed data (these data are more available than pesticide data).

When the model is to be applied to any real situation, the model user should always bear in mind the assumptions made in the development of the model. The assumptions in the Rosemaund model have been outlined and their significance assessed. Given appropriate care the Rosemaund model could be applied to other catchments, indeed to gain confidence in its predictions it should be applied and tested on a number of different catchment types.

5.2.5 A Simplified Application of the Pesticide Model for Catchment Management

One of the uses of a model such as that described here is to help in designing a sampling strategy to monitor effectively and economically pesticide runoff from catchments. Also, knowledge of pesticide concentrations is important when measuring or anticipating environmental impact. A routine sampling programme can be more effective if it is set up with some prior knowledge of when runoff is likely to be a problem. In this section a hypothetical case study will be used to illustrate one possible use of models to help in the setting up of sampling strategies.

The model was used to simulate concentrations of isoproturon leaving the Rosemaund catchment as a result of two separate applications of the chemical to a total of 50 ha (approximately one third of the catchment). The first application at a rate of 0.5 kg/ha was made on 1 October 1992 and the second on 1 November 1992 at the same rate, 25 ha being treated on each occasion. Hourly rainfall and daily evaporation estimates were taken from the Automatic Weather Station. All other parameters in the model were as for the model calibration and simulations described in Section 5.2.1 above.

A plotting program was used to generate plots of daily maximum and mean daily values of isoproturon leaving the catchment. The same program calculated the length of time (relative to the first application) required for concentrations of these variables to fall permanently below certain threshold values. Table 5.5 gives these timings for the threshold values chosen

for the scenario described above. The maximum pesticide concentration predicted over the entire period was 169 µg/l with a maximum daily mean value of 51 µg/l.

Table 5.5 **Time taken for daily maximum and mean daily isoproturon concentrations to fall below threshold values.**

Threshold Concentration (µg/l)	Time after application (days) required to reach thresholds expressed as;	
	Mean Daily Concentration	Maximum Daily Concentration
0.1	157	185
0.2	140	141
0.5	122	123
1.0	114	116
2.0	103	105
5.0	81	82
10.0	67	67
20.0	47	58
50.0	42	55

Information such as this can be used to help in designing a sampling programme to reflect true levels of pesticide contamination in the environment. Sampling intensity can be altered through the year to reflect declining pesticide concentrations with perhaps a suspension of sampling after a certain threshold is likely to be passed (including a suitable safety margin). The numbers in Table 5.5 would be different for each pesticide used within a catchment. Calculation of threshold values for all chemicals used could be used to determine their inclusion in a sampling programme or not. Further, chemicals could be removed from analysis suites as their predicted levels fall below established environmental quality standards. From the water treatment point of view, knowledge of predicted peak and duration of pesticide concentrations in raw water abstracted for potable supply would be very valuable information. For example, such knowledge might allow the more efficient use of tertiary treatment (such as activated carbon) to reduce pesticides to below MAC levels.

In order to generalize the approach to other catchments of a similar size to Rosemaund, the model needs to be thoroughly tested and confidence in its predictions established. For such tests a good knowledge of pesticide application rates and timings is also necessary as is a time series of typical rainfall and evaporation. To change scale and move up to water supply catchment scale there will be a need to integrate source area models with river routing models. This would enable diffuse pesticide pollution to be introduced into conventional water

quality models as point sources. Such an approach would take care of the distributed nature of the pollution and time of travel effects on pollution dilution as it moves through the river network.

5.3 Other modelling work at Rosemaund

The data generated at Rosemaund is being used to attempt to validate several different models by a number or groups. While it is not within the scope of this report to present the detailed results of other workers a brief overview of the work can be given particularly where there is a formal link with the IH/NRA study.

5.3.1 Building Research Establishment

The modelling efforts of the BRE are being pursued jointly with MAFF in order to develop a model that may be of help in the registration of new pesticides. The results of the modelling to date have been reported elsewhere (Brooke and Mattheissen, 1990; Williams *et al*, 1991) and only a summary will be presented here.

The model used is based on the second level of Mackay's development (Mackay and Paterson, 1981). It uses simple physico-chemical properties of the pesticide to calculate how it partitions between a number of idealised phases or compartments of the environment and hence is appropriate for new pesticides for which limited data are available. Processes which remove the chemical, such as degradation or water flow, are also included. The model has been modified to follow the time pattern of distribution, rather than calculate an equilibrium situation for a constant input. For this particular case, two linked models were used. The first of these was the field itself, and was made up of soil, soil water and air over the field. The dimensions and properties of each phase were derived from measurements at the site. When the chemical is added to the model, it partitions between the three phases. The removal processes then act on the appropriate phase for a set period, usually one hour; the amount of chemical remaining is then repartitioned and new concentrations calculated. Rainfall is used to model the water flow through the field, carry chemical out of the field model and provide the link to the second model (the stream). The stream model consists of five phases: air, water, sediments, suspended sediments and biota. Water from the field model enters the stream carrying the chemical with the input set back in time to allow for the delay in stream rise following rain. Partitioning and removal work as for the field model.

The model always over estimated the amount of pesticide reaching the stream and estimates were up to several orders of magnitude greater than observed values. The simulations were improved if some effort was made to include the hydrological response of the system. This was done by using a runoff coefficient to determine the amount of rainfall reaching the stream or drain.

5.3.2 SoilFug

SoilFug is another development of the fugacity models of MacKay (Mackay, 1979; Mackay and Paterson, 1981). A full description of the model is given elsewhere (Di Guardo *et al*, 1993). The model is essentially an non-steady state but equilibrium event model. It takes into account the disappearance of the chemical according to different phenomena (degradation, volatilization, runoff) but then calculates the partition among the different phases of the soil using a level one fugacity model. The model seeks to estimate the flow weighted average concentration that occurs as the result of a rainfall event. The hydrological response of the system is accounted for by using actual measured (or estimated) runoff amounts for each event.

SoilFug represents the catchment by a soil box and a stream box. The soil box is divided into four compartments, soil, soil organic matter, soil water and air. When pesticide is applied to the soil it is distributed between these compartments such that the fugacities become equal. Fugacity is the tendency of a compound to escape from one phase/compartment to another with chemical moving from high fugacities to low fugacities. The fugacity of a given chemical in each phase can be related to physico-chemical properties of the chemical. For example the fugacity of a chemical in soil organic matter is dependent on its adsorption coefficient in organic matter, in soil water on its solubility and in air on its vapour pressure.

From the original distribution, the chemical is degraded by biological activity and volatilised out of the soil. At each time-step a new equilibrium distribution based on the new fugacities is calculated and the whole process continues in the next time step. When a rainfall event occurs the rainwater is mixed with the existing soil water and a new equilibrium is formed. The runoff generated by the event then carries the pesticide (with a concentration equal to that of the soil water) out of the soil into the stream box. Here it is mixed with water from other untreated parts of the catchment to produce a catchment output concentration. The processes of decay and redistribution are then continued until the next rainfall event.

Results of a large range of simulations of Rosemaund data are summarized in figure 5.7, whilst details of the model applications and a full discussion of the results are available in Di Guardo *et al*, 1993. The model performed well with estimates of pesticide concentrations (for neutral or un-dissociated pesticides) better than one order of magnitude in 38 of the 50 events modelled. The tendency of the model was to over predict observed mean concentrations.

The model benefits from the fact that it is easily applied to new catchments requiring only the most easily available data for its application. A typical application requires the following data:

1) Catchment area, pesticide application areas and rates.

2) Soil physical properties, namely temperature, soil depth, air volume fraction and water volume fraction at field capacity, and organic carbon fraction.

3) Physico-chemical properties of the pesticide, namely molecular weight, water solubility, vapour pressure, k_{oc} and half life.

4) Rainfall amount in event, runoff resulting from rainfall, and time between pesticide application and rainfall event.

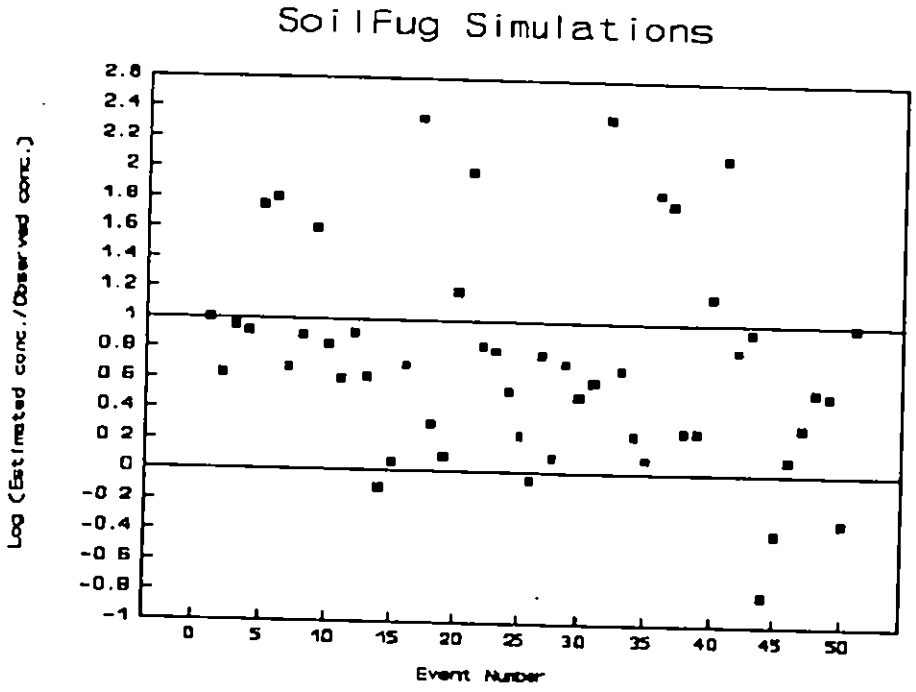

Figure 5.7 **Logarithm of the ratio of estimated to observed concentration for each of the event/pesticide/site combinations simulated. Points between the 1 and -1 lines on the Y-axis are deemed to be good simulations.**

The model is available as a user friendly Windows™ application which, combined with its ease of application to different catchments, gives it great potential as a screening tool for assessing the likely environmental concentrations of pesticides in surface waters. However, while it's ease of portability between catchments may make its use easier than the Rosemaund model, SoilFug only estimates average concentrations and therefore can give no information on the magnitude or duration of pesticide peaks, which can be done with the Rosemaund model. SoilFug is clearly an attractive option for use in an organization like the NRA and it is recommended that it be included in any further testing that might be considered for the Rosemaund model.

6. DISCUSSION AND CONCLUSIONS

The Rosemaund study has established that the use of pesticides, even when applied according to good agricultural practice, can lead to the contamination of surface waters in the catchment into which they drain. The magnitude of the concentrations observed in surface waters varies, not only between pesticides, but also between rainfall driven events. However, whenever rainfall occurs following a pesticide application, some of that chemical will be transported to the stream. One of the reasons ADAS Rosemaund was chosen was because its soil type and geology meant that the hydrological regime was likely to be surface water dominated. In this respect it is perhaps not surprising that rainfall transports pesticide from the soil to the stream. However, this type of highly structured soil with underdrainage forms 45% of agricultural land of the UK (Cannel et al, 1978). Thus while the results from this study may represent a worst case in terms of surface runoff concentrations, they are of great significance to the NRA, private water companies and for agriculture in general.

The mechanisms of pesticide movement with respect to their physico-chemical properties and the soil hydrological pathways have already been discussed in Section 4. It is worth repeating that rainfall events generate flushes of pesticide which reach the stream coincident with or slightly ahead of the main surge of water. This gives rise to high but short lived concentrations in receiving waters. The significance of these concentrations to aquatic life will obviously depend on the toxicity of the pesticide, the duration of exposure and the robustness of the organisms of concern. However *in situ* bioassays conducted by MAFF in the stream at Rosemaund have shown observed carbofuran concentrations to be fatal to the fresh water shrimp (*Gammarus pulex*), (Matthiessen *et al.*, 1993). It is clear that transient, high pesticide levels in headwater catchments, resulting from the use of products at approved rates, are of potential significance to the ecology of streams. Some account of such transient exposures (and potential bioaccumulation) needs to be built into future pesticide assessments if headwater catchments are to be protected fully. Protection of the headwaters of streams should ensure protection of habitats throughout the river network from diffuse pesticide pollution, as dilution, degradation and sorption of pesticides on to sediments reduces their maximum concentration.

Of particular concern is that these high concentrations of pesticide are generated at the sub-catchment level by very small amounts of leached pesticide. In the Rosemaund study the estimated maximum transfer of pesticide to the stream in a single event was 60.6 g and the maximum amount as a percentage of pesticide applied was only 1.1 %. It is almost inevitable that such small amounts will be lost from any catchment where pesticides are used, whatever the agricultural practice. It is the short duration pulses of peak pesticide concentrations, demonstrated so clearly in this study, which are of potentially greatest environmental concern. The implication here is that, while modern chemical based agriculture is practised, the NRA must accept that pesticides at significantly high concentrations will reach surface waters at the sub-catchment level. The duration over which the risk of pollution by peak concentrations exists may be reduced, but probably not eliminated, by using chemicals that are rapidly degraded. However, such chemicals will by their nature have little residual pesticidal effect and may therefore result in multiple applications where before one would have sufficed.

The concentration of the highly sorbed herbicide, trifluralin, has been measured in the dissolved and particulate phases in samples from three rainfall driven runoff events. These

measurements have shown that in the majority of cases the dissolved fraction carries more than 50 % of the pesticide load. This is because the mass of water moving from the fields is so much greater than the mass of sediment. As a first approximation, even pesticides as sorptive as trifluralin (k_{oc}= 8000 ml/g) may be considered to be transported in the dissolved phase. However, a small amount of trifluralin will be transported on particulates to the stream where some will be deposited on the stream bed. Pesticides so deposited might become bio-available, either through desorption in to the water column, or ingestion by benthic feeders resulting in possible bio-accumulation. However, such considerations were outside the scope of this study and there is a need for further work in this area, which might include; sediment bioassays, sediment desorption and bio-accumulation studies.

The above discussion is most relevant to small headwater catchments where the main land use is for agricultural production. Looking at the larger catchment scale it is likely that, in most catchments, the proportion of land used for crop production will be less. Thus a dilution of pesticide load would occur and this dilution is the first line of defence in preventing high concentrations occurring in main rivers from which most potable abstractions are made. There is clearly a need to assess the extent of pesticide usage in water supply catchments with a view to estimating a maximum acceptable usage (MAU). The MAU would be set to guarantee both the quality of raw waters used for potable abstraction and to meet any environmental quality standards that may exist.

The only practicable way to move towards an estimate of maximum acceptable loads is through the use of models. A combination of models would be required to achieve this including a model to estimate diffuse runoff from source area catchments and a river network model to integrate the inputs throughout the extent of the catchment. The source area model would require reasonably accurate data on pesticide usage within the catchments as it changes from year to year. It is unlikely that actual data would be available for whole catchments and so estimates would have to be made based on cropping patterns and general pesticide use. In this respect the WRc pesticide usage model FARMSTAT might provide the necessary data, although it only works on a retrospective basis and its use for predictive modelling would have to assume some consistency in pesticide usage from year to year.

Once such a modelling structure was set up for a particular catchment it would prove a powerful tool for a variety of additional applications. For example a pesticide sampling strategy may be developed which could provide a true picture of pesticide contamination in the most cost effective way. The location of pesticide 'black spots' could be predicted and targeted for increased monitoring. The use of different groups of pesticide is seasonal and the pesticide analysis suite could be tailored to meet predictions of the temporal variability of pesticides within a year.

The pesticide model developed in this study has shown itself to be a good predictor of pesticide concentrations at Rosemaund. It has yet to be tested elsewhere and its portability to other catchments is therefore yet to be proven. The assumptions and limitations of this model have been discussed in Section 5.2.4. Perhaps its most limiting feature as regards all year assessments is that it is only valid under conditions of winter and early spring drainage. However, these are the periods of peak pesticide usage when surface waters are at most risk from pesticide runoff and therefore this should not prove to be a problem. Section 5.2.3 showed how the model might be used to give guidance on establishing a sampling programme

for Rosemaund using isoproturon as an example. If a threshold value can be defined below which isoproturon concentrations are considered to be acceptable, then the number of days after application when this condition will arise can be estimated. After this date, sampling for isoproturon could be reduced or suspended. A similar approach, using this model, could be applied to other catchments and for other pesticides.

A new fugacity model, SoilFug, has been tested on the Rosemaund data and good agreement has been obtained (see Section 5.3.2). This model simulates the mean concentration of pesticide in runoff water resulting form rainfall events. In 50 simulations of neutral or undissociated pesticides, 36 were estimated to within one order of magnitude of the actual concentrations. The parameters required by this model, in order that it can be applied on new catchments, are generally easy to obtain or estimate from existing procedures.

While a complex model, with its explicit links between the physico-chemical properties of the pesticide and the hydrological flow paths, was the desired end product of this study, there is a half way house represented by empirically derived indices of pesticide contamination. One such index, based on half life and the timing of rainfall events after application, has been developed for the Rosemaund data (see Section 4.2.3). This approach gives quick, easily calculated estimates of when pesticides are likely to be a problem. Although there was no well correlated relationship between the index given in section 4.2.3 and maximum pesticide concentration, there was a qualitative increase in the observed concentration with increasing value of the index. The general problem with empirical relationships is that they are not valid outside the range of data for which they were estimated and should not therefore be used for other locations.

Finally, it must not be forgotten that pesticide usage is not the only variable in the pesticide runoff equation over which man has control, agricultural practice may be a key influence. The type of crops grown and the way in which they are grown could have significant effects on the amount of pesticide that is transported to streams. If models are to give a complete picture of the pesticide story then they must build in links between agro-practice and pesticide runoff. This link might primarily be concerned with the different water pathways that are promoted by a range of cultivation methods and how this changes the interaction between the soil and the pesticide.

The Rosemaund pesticide study has produced one of the best data sets on the field and catchment scale movement of pesticides in the UK. This has been due in no small measure to the foresight of the MAFF, BRE, NRA and IH in establishing a collaboration at ADAS Rosemaund. This data set has allowed an improved understanding of how pesticides move to surface waters and the environmental concentrations that result from this movement. This has allowed existing and new mathematical models to be developed and tested using the data and their performance to be assessed. The outputs from this project have taken our knowledge of pesticide behaviour a major step forward and have laid the foundation for more accurately predicting pesticide behaviour and targeting pesticide monitoring programmes.

7. STRATEGIC RECOMMENDATIONS

The research carried out by the Institute of Hydrology and collaborating organizations has led to a significant advance in knowledge of pesticide runoff mechanisms and resulting surface water concentrations. The nature of the Rosemaund catchment has directed the research towards underdrained, structured soils, which arguably represent a worst case scenario for pesticide runoff. However this soil/drainage type represents a significant fraction of cereal production land in the UK and is therefore of great relevance to the NRA. There are a number of observations and recommendations that can be made based on the work carried out to date.

1) The use of pesticides in agricultural production will inevitably lead to the contamination of any stream that drain the area of their use. In particular rainfall events will cause short lived peaks in pesticide concentration to occur in surface waters. The prediction of these peak concentrations is complicated but will depend on the amount of pesticide used, the proximity of the rainfall event to the application date, the degradation rate and sorption coefficient of the pesticide and the antecedent soil moisture conditions. The conclusions from this study particularly apply to soluble pesticides with low sorption characteristics. however, initial results from Rosemaund also indicate that a large proportion of the load of supposedly highly sorbed chemicals is transported in the dissolved phase and therefore may be treated similarly to less sorbed chemicals.

2) If environmental quality standards (EQS) for pesticides are to be set for all water courses then monitoring programmes will have to be established to assess compliance with such standards. If catchments fail EQSs then some change in pesticide usage may be necessary. The application of a pesticide runoff model, such as that developed for Rosemaund, can help in both of these management activities. It will enable targeting of monitoring to critical periods of pesticide occurrence and will, where necessary, provide the evidence to demonstrate the need for changes in agricultural practice.

3) The significance of pesticide concentrations leaving agricultural catchments needs to be assessed at two levels. Firstly in terms of the toxicological effects on the aquatic fauna inhabiting streams in agricultural areas including possible bio-accumulation in the food chain. Secondly, with respect to public water supply abstractions and achievement of legislated maximum acceptable concentrations in potable water supplies.

4) An efficient sampling strategy must target monitoring programs to the peak application periods of autumn and early spring, particularly as this is the period when soil water contents are high, in the UK, and pesticide runoff likely. If peak concentrations are of concern, because they are most likely to cause environmental damage, then some sampling should include the capture of rainfall events.

5) In order to manage agricultural catchments effectively there is a need for a greater understanding of the link between general agricultural practices (other than pesticide usage, eg. ploughing, planting) and pesticide runoff. Only by establishing such links can management strategies to reduce pesticide run-off reduction be explored. A review

of research in this area should be carried out with a view to suggesting which aspects of agro-practice have most influence on pesticide run-off.

6) There is a need for the Rosemaund and SoilFug pesticide models to be tested on other catchments so that their wider application and thus usefulness to the NRA, can be established. This testing of the models should include different soil types and larger catchments and might be achieved using existing data sets if available.

7) The software for the Rosemaund model has been supplied to the NRA together with model documentation. The NRA must establish to what extent the model should be validated before it is released for more general use within the NRA. Guidance should also be given on when the model should be used and in what circumstances.

8) The modelling of pesticide run-off in very large catchments (water supply size), will require the linking of a number of generic models. Models like the Rosemaund model which are applicable to smaller headwater catchments and their outputs, should be fed into a river network model. This approach should allow for the different travel times from various parts of the catchments and any in-stream purification processes that may occur down the river system. Such a multi-modelling approach is being developed for the rivers of North East England by IH as part of the Land Ocean Interaction Study (LOIS), a NERC community programme. The LOIS programme may lead to development of a catchment scale model for transport and fate of many chemicals, including pesticides.

9) It is recommended that a pilot study should be set up where such an approach might be applied to 2 or 3 test catchments. The study should link predictions of pesticide use (eg from FARMSTAT) to sub-catchment runoff models (such as the Rosemaund model), which in turn would link through to river network routing models (eg QUASAR), to give predictions of pesticide concentrations at key locations in the catchment. Validation of such predictions could then take place.

10) Another simpler approach would be to use the proposed index of pesticide runoff, I_m, as a crude indicator to establish whether or not pesticide concentrations are likely to be a problem in surface waters in agricultural catchments. However, caution should be exercised in interpretation of the index value, as it is an empirical relationship developed from data on only one catchment.

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Appendix 3 Sediment controls on the Riverine Transport of Herbicides: A pilot study on the River Windrush, Cotswolds, UK

Sediment Controls on the Riverine transport of Herbicides:

A pilot study in the River Windrush , Cotswolds, UK.

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FINAL REPORT ON NERC GRANT GR9/637

Source-sediment controls on the riverine transport of herbicides : a pilot study in the River Windrush, Cotswolds, UK.

Field location and sampling

The River Windrush flows NW-SE, rising from Jurassic carbonate-fed springs and streams near Guiting Power and joining the River Thames at Newbridge (Fig. 1). The river sediment is derived in large part from the catchment bed-rock and is therefore carbonate dominated (Middle Jurassic) in the upper reaches, clay dominated (Lower Lias) in the middle reaches, and mixed (carbonate and clay) in the lower reaches. Three sampling sites were selected to represent each of the river-sediment types (Fig. 1) : site 1, Harford Bridge (Brit. Nat. Grid Ref. (NGR) 129228), site 2, Dickler (NGR 181197), site 3 (NGR 403014). We originally intended to sample six sites but the very low concentration of suspended sediment led us to concentrate our efforts on three sites. In addition source rocks were sampled at NGR 177221 (Lower Lias Clay) and NGR 298102 (Middle Jurassic carbonate 'White Limestone')

All samples were collected on 02.04.92, starting at site 1 and moving down-stream. Standard precautions were observed in the preparation of the sampling equipment and the inclusion of control blanks from the sampling through to the final analysis. Water samples were collected for pesticide analysis in pyrex bottles fitted with PTFE screw caps. Further samples were collected for major-ion analysis; pH, temperature, conductivity and oxygen concentration were measured in-situ. Approximately 32 litres of water were collected in glass demijohns at each site for the separation and analysis of suspended sediment. Surface bed-sediments to a depth of ca. <5 cm, were collected using either a stainless steel scoop or using a pond net (1 mm mesh). The sediments were immediately transferred through a 1 mm screen into glass jars with tops lined with aluminium foil. Very fine particulate material associated with the bed-sediment that remained in suspension was stored separately in glass demijohns. This was later centrifuged and combined with the rest of the bed sediment. The water samples were immediately extracted with solvent, the bed sediments were freeze-dried until the weight loss was <0.1% in 24 h; the samples of suspended solids were stored in the dark at ca. 5°C and the solids separated over the following 5 days using an MSE 18 centrifuge with a continuous-flow-rotor operated at 110-120 ml/min.

Laboratory Analysis

The water samples were extracted (Lopez-Avila et al., 1990) with dichloromethane (DCM) with Kuderna-Danish (KD) concentration and a solvent change to 5% acetone in hexane. The freeze-dried sediments (10g) were soxhlet extracted for 5 h with 60 ml of DCM. The extracts were then concentrated using KD apparatus and the solvent changed to 5% acetone in hexane. The extracts were analysed using a Perkin-Elmer 8700 instrument with split-splitless/PTV injectors, an electron-capture-detector (ECD) and nitrogen-phosporus thermionic detector (NPD) with confirmation of the pesticides by gc/ms in selective-ion mode. The samples were analysed for the following compounds: α HCH, γ HCH (lindane), p,p' - DDE, p,p' - TDE, dieldrin, endrin, heptachlor, DDT, cis/trans-permethrin, cypermethrin, fenvalerate, deltamethrin, atrazine, simazine, prometryn, malathion, parathion, fenitrothion and dichlorvos. The limits of determination were ca. 1.0 µg/kg and ca. 10 ng/l for the synthetic pyrethroids and ca. 0.1 µg/kg and 0.5 ng/l for the other compounds for sediment and water analysis

respectively. The organic carbon content (OC) of the source sediments, WLS and LLC, bed and suspended sediments was determined by combustion and corrected for inorganic carbon. X-ray diffraction was carried out on the source, bed and suspended sediments using a Philips PW 1380 horizontal goniometer with PW 1710 diffractrometer control. The specific surface areas of the freeze-dried sediments were determined by nitrogen gas adsorption using a flow-technique with overnight outgassing at 110°C and analysis by the single-point BET method. The sediments were examined using scanning electron microscopy (SEM).

The adsorption of parathion, malathion, fenitrothion, atrazine, simazine and prometryn at 10 ± 0.2°C was determined simultaneously using a batch procedure; the adsorption of parathion was studied separately using a flow-cell (FC) described previously (House and Farr, 1989). In brief the batch method (BM) involved the addition of freeze-dried bed sediments to 220 ml of 0.01 M $CaCl_2$ containing 3-30 x µg/l of each pesticide (adsorbent concentrations of 0.03-0.14 kg/l depending on the adsorption affinity of the sediment).

Results and Discussion

The field pH values were 8.4, 7.7 and 8.2 at sites 1 to 3 with oxygen concentrations between 79-105% saturation and water temperatures between 6.8 and 7.3°C. The major-ion analysis showed the waters to have similar compositions with calcium concentrations of 2.4-2.7 mM. The suspended sediment concentrations were 5.1, 26.4 and 13.7 mg/l for sites 1-3 respectively.

Pesticide analysis of the field samples (Table 1) showed that the traizines were found in all the waters but not in the sediments. Parathion was in all the sediments with the concentrations in the suspended sediments much higher than in the bed-sediments. Five organochlorine compounds were detected, with concentrations in suspended sediment generally more than an order of magnitude higher than in the bed-sediment. Cypermethrin was the only synthetic pyrethroid detected.

The results of the sediment characterization are given in Table 2, and corresponding SEM photomicrographs are illustrated in Plate 1.

The results of the batch adsorption experiments are given in Table 3 expressed as the distribution coefficients normalized with respect to organic carbon, K_{oc} and specific surface area, K_d/Σ. The results from the flow-cell obtained after 1 h contact between parathion and the bed-sediments have K_d values of 98, 19, 53 and 99 l/kg for LLC and sediments from sites 1-3 respectively. The pH during the batch adsorption experiments was ca. 8.5 for WLS and between 7.6 and 7.9 for the other sediments with an oxygen saturation >79%. The final solution compositions of the supernatants were also determined. Both nitrate and phosphate leached from the sediments to produce concentrations of 2-4 mM and 0.1-4 µM respectively with the highest concentrations from sediment 3; the final concentrations of calcium differed <10% from the original values with traces of Mg, Na, K also present.

The relationships between the composition of the source and bed/suspended sediments and their application for the prediction of OC and $K_d\Sigma$'s may be elucidated further using the equation:

$$\text{Fraction of LLC in sediment} = [\, P(sed) - P(WLS) \,]/[\, P(PLLC) - P(WLS) \,]$$

where P(sed), P(WLS) AND P(LLC) are the percentage by mass of the mineral components in the sediment, WLS and LLC respectively. This was attempted with

quartz, calcite and kaolinite as the predictive minerals, P(sed), and the linear combinations necessary to produce the correct sediment compositions were determined. In general illite was always underestimated with more in the sediments than can be explained by a linear combination or multiple regression using WLS and LLC as the predictors. For site 1, kaolinite gave the best prediction for OC and the K_d' s for fenitrothion, malathion and parathion with similar combinations of source sediments (ca. <0.1 LLC and >0.9 WLS). It was the only site for which the prediction of OC in the bed-sediment was greater than the observed value. At site 2, only quartz was able to predict the composition (ca. >0.8 LLC and <0.2 WLS) but underestimated all the clay fractions. In contrast quartz, calcite and kaolinite were all reasonable predictors for site 3 (ca. 0.6 LLC and 0.4 WLS). The OC was underestimated but the K_d for malathion was in agreement with the experimental value (Table 3). The influence of the source sediments at sites 1 and 2 was evident viz site 1 was dominated by WLS, site 2 by LLC, with more integrated sediments downstream at site 3.

The K_{oc}' s for LLC and the sediments from sites 2 and 3 (Table 3) were within the range reported by Karickhoff (1981) for soils. The correlation between the K_d' s and the composition of the bed-sediments revealed that the adsorption affinity of parathion correlated well with the triazines and fenitrothion but not malathion. There was also a good correlation between the flow-cell results for parathion and the other pesticides except malathion. This suggested fundamental differences in the adsorption mechanism for malathion which has a distinctly different molecular structure from fenitrothion and parathion. The lower values of K_d from the flow-cell indicated significant kinetic effects probably associated with diffusion of the pesticides into the bulk matrix. An excellent correlation between the K_d for malathion, clay content and Σ (K_d = 2.85 + 7.20 (± 0.50) Σ; R = 0.993; the standard deviation of the slope is shown in brackets) was evident. In contrast, the correlation with OC was poor (R = 0.678) for malathion but good for both parathion and fenitrothion (K_d = 5.0 + 50.9 ± 13.6 OC; R = 0.91 and K_d = 15.4 + 37.4 (± 8.4) OC; R = 0.93 respectively). A reasonable correlation between the concentration of parathion in the sediments and the OC was also found (R = 0.902) which suggested that the concentration of parathion in the water was similar at all the sites but below the limits of determination of our method, i.e. at a lower concentration than was expected from the laboratory adsorption studies. The specific surface areas correlated best with the individual clay fractions particularly kaolinite, R = 0.99, and the expandable clays, R = 0.97, but very poorly with OC, R = 0.65.

The high K_{oc}' s for the bed-sediments from site 1 indicated that the partition of the pesticides with this OC was not consistent with the partition behaviour with the OC in other sediments. In contrast, the values of K_d/Σ for this sediment were in the range found for the other sediment, suggesting that the exposed surface of this sediment was a key influence on the pesticide interaction. Similarly, the sorption of malathion with K_d/Σ = 8.4 ± 1.5 µm for all the sediments, appeared closely related to the exposed surface area of the sediments rather than to the OC content. The only sediment showing the traditional linear relationship viz (standard deviation of coefficients shown in brackets):

$$\log K_{oc} = 1.34(0.26) + 0.655(0.09) \log K_{ow} ; R = 0.975,$$

was that from the downstream site 3. However, a good correlation:

$$\log K_d/\Sigma = -1.00(0.27) + 0.66(0.09) \log K_{ow} ; R = 0.973,$$

for site 3 sediment was also found which suggested that the interaction of the pesticides was with a surface film rather than partition with discreet organic particles.

Conclusions

1. Ten different pesticides were detected in the River Windrush, belonging to four groups; triazines, synthetic pyrethroids, organochlorines and organophosphorus compounds.

2. The triazines were found in the waters, but not the sediments, whereas in general the other detected pesticides were more concentrated in the sediment. In particular, suspended-sediment pesticide concentrations were often more than an order of magnitude higher than in corresponding bed sediments.

3. The mineralogy of the river and source sediments is an important factor in controlling the adsorption of the pesticides studied. Organic carbon content and specific surface area are also significant.

4. Catchment geology would appear to be a good and rapid guide to pesticide transport behaviour in river systems.

Outlook

The sampling and detailed analysis carried out in the pilot project has allowed an important advance in our knowledge of the environmental behaviour of pesticides; sediment composition has been shown to exert a powerful influence on pesticide transport and concentrations. The work clearly demonstrates a need to investigate a wider range of source sediments and to include other pesticides in the study.

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Lopez-Avila, V., Wesselman, R. and Edgell, K. (1990). Gas chromatographic-electron capture detection method for determination of 29 organochlorine pesticides in finished drinking water: collaborative study. *Journal of Association of Analytical Chemists*, 73, 276-286.

TABLE 1 Concentration of pesticides in samples from R. Windrush. (C : confirmed by gc/ms, T : trace detected, - : not detected).

	Compound	Water ng/l				Sediments ug/kg Bed			Sediments ug/kg Suspended		
		1	2	3	4	1	2	3	1	2	3
Organochlorines	lindane	-	T	0.7C	5.9	-	-	-	-	-	-
	DDT	2.8	T	-	-	0.2C	-	-	T	1.1	4.7
	DDE	-	-	T	-	T	0.2	0.2	T	1.6C	3.7
	heptachlor	-	-	-	-	-	0.1	0.2	13C	5.1C	4.7
	dieldrin	-	-	-	-	-	0.2C	0.2C	17C	8C	12
Triazines	simazine	4.9	1.5C	22C	26C	-	-	-	-	-	-
	atrazine	15C	7C	17C	32C	-	-	-	-	-	-
	prometryn	-	-	1.2C	4.4	-	-	-	-	-	-
Organophosphorus	parathion	-	-	-	-	0.3C	0.6C	1.0C	13C	3.3C	8.8C
Synthetic pyrethroid	cypermethrin	-	70	-	-	-	-	-	-	-	-

TABLE 2 Specific surface area, Σ, and percentage composition by percentage mass of organic carbon, OC, and crystalline components of the sediments. (Clay mineral analyses are totalled to 100%).

Sediment	OC	Σ $m^2 g^{-1}$	Q	C	K	I	E	F
LLC	3.1	15.5	77	13	47	-	53	-
WLS	0.09	1.8	-	99	16	40	64	-
Bed 1	0.1	3.6	53	42	27	27	46	3
2	3.5	29.1	69	2	42	24	34	8
3	4.7	10.0	45	45	39	24	37	3
Susp 1	12.9	20.5	58	34	30	37	33	7
2	7.1	13.5	39	3	42	42	36	6
3	7.4	18.3	45	29	42	36	22	3

Quartz (Q), calcite (C), feldspars (F) determined by whole rock analysis; kaolinite (K), illite (I) and expandable clays (E) from the clay analysis. Key: = not detected, LLC = Lower Lias Clay, WLS = White Limestone.

TABLE 3 Results of the batch adsorption experiments at 10°C.

	simazine			atrazine			prometryn		
	c	K_{oc}	K_d/Σ	c	K_{oc}	K_d/Σ	c	K_{oc}	K_d/Σ
LLC	10.4	128	0.26	11.1	96	0.19	4.6	320	0.65
WLS	10.8	-	-	10.9	-	-	10.9	-	-
1	9.3	7000	1.9	9.4	7000	1.9	9.9	1000	0.28
2	9.1	171	0.21	9.6	171	0.21	6.2	200	0.24
3	4.2	702	3.3	4.2	872	4.1	3.4	808	3.8
	fenitrothion			malathion			parathion		
	c	K_{oc}	K_d/Σ	c	K_{oc}	K_d/Σ	c	K_{oc}	K_d/Σ
LLC	0.4	5256	10.6	0.3	3782	7.6	0.4	5160	10.4
WLS	6.2	-	-	3.7	-	-	6.7	-	-
1	1.8	37000	10.2	1.1	38000	10.5	2.1	38000	10.5
2	0.8	2943	3.5	0.2	5943	7.2	0.8	3086	3.7
3	0.5	4298	20.2	0.7	1723	8.1	0.4	6404	30.1

c (µg/l) denotes the concentrations of pesticide in solution after 24 h mixing with sediments. K_{oc} is in l/kg and K_d/Σ is in units of µm.

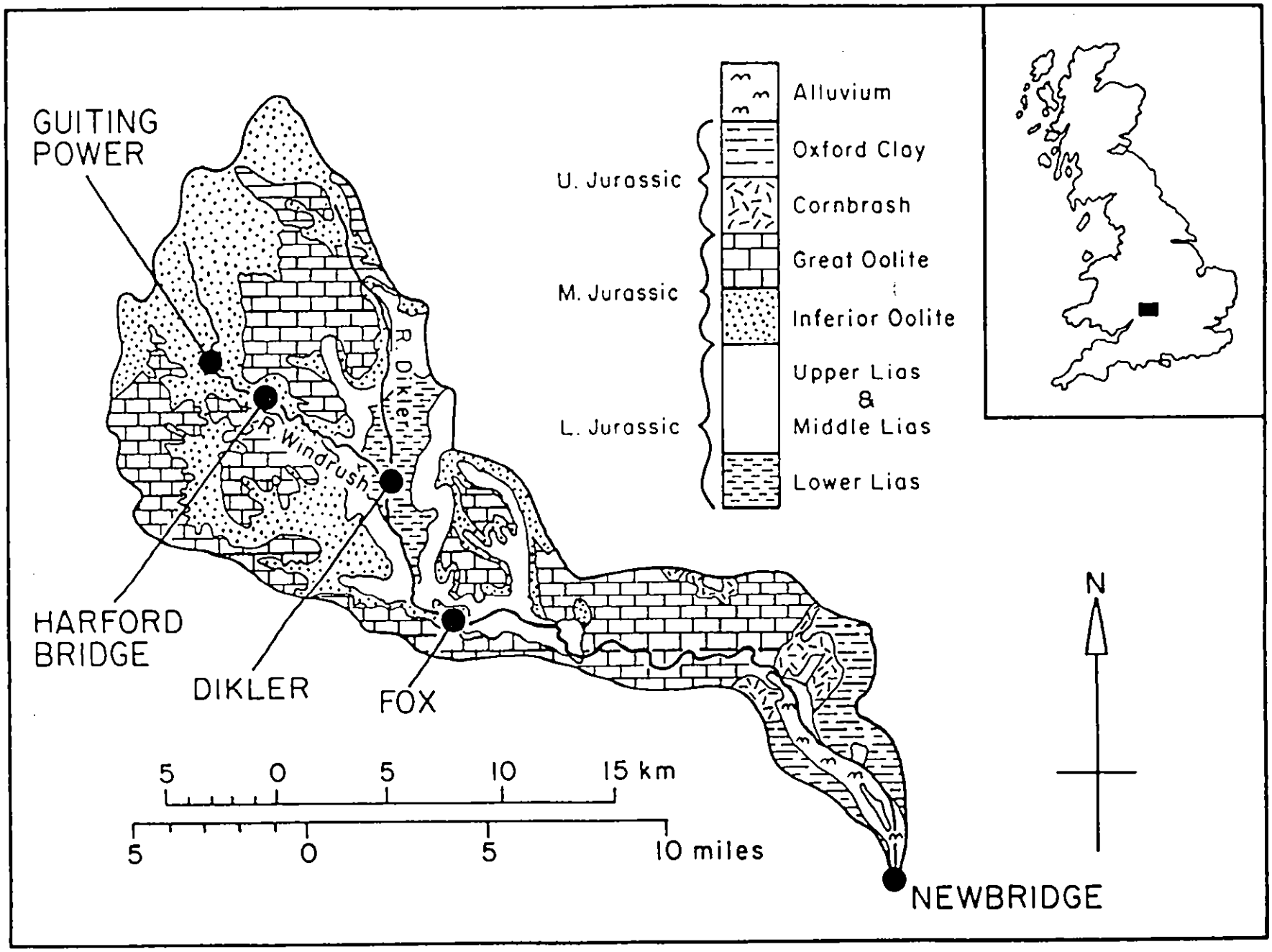

Fig. 1. Study area showing the geology of the catchment and the location of sampling sites.

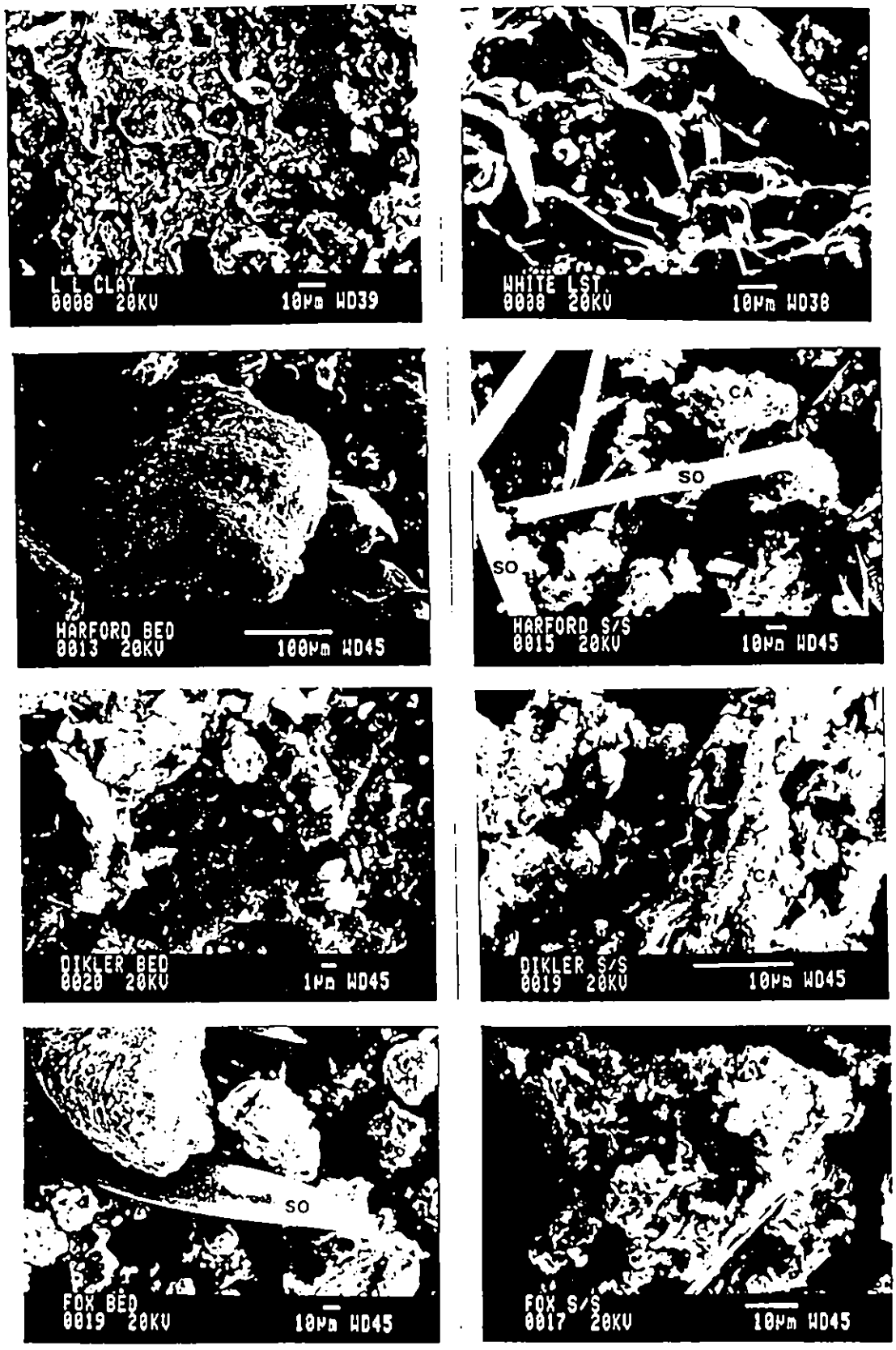

Plate 1. SEM photomicrographs of R. Windrush bed (<1mm) and suspended sediment, (Harford, site 1; Dikler, site 2; Fox, site 3). Note the siliceous organic components (SO) (eg Harford suspended sediment)and the high percentage of clay aggregates (CA) in the suspended sediment.

Appendix 4 Conservation and pesticide drift

7 Conservation and pesticide drift

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7.1 Introduction

The first six Chapters of this book were written by the researchers who had been contracted by NCC/EN and DoE over the last six years or so to provide information on drift. The composition of each Chapter is similar to the contributions presented by their respective authors at the Seminar in February 1992 (see the Foreword). This Chapter is different in that it has been compiled for the specific purpose of pulling the work together and rounding off this book. One of its aims is to review the work, principally from the point of view of the conservationist but also in a way that will be of relevance for the manufacturer, user or regulator of pesticides. In doing this, attention is briefly drawn to the work described in more detail in the preceding Chapters. However, I also deal more fully with certain aspects that have not been covered in detail elsewhere in the book.

7.2 The spray drift programme

7.2.1 Identification of pesticides of concern

The initial contract review (Williams *et al* 1987) focused entirely on the impact from herbicides and insecticides. It was reasoned that herbicides would have the greatest impact on wildlife habitats generally, as well as on individual species of plants of conservation interest. Effects on plants are also likely to cause indirect effects on animals that depend on them for food or shelter. The other group of pesticides of concern was the insecticides. Insecticides are likely to be lethal to a range of terrestrial insects and other invertebrates. Terrestrial invertebrate fauna is an important component of many reserves. Direct effects on invertebrates might lead to indirect effects on other organisms, for example their vertebrate predators. Some insecticides are also acutely toxic to freshwater life, such as fish and particularly invertebrates (Table 7.1). Although insecticides, especially the organochlorines, have in the past caused widespread and significant effects on terrestrial vertebrate wildlife, recently-approved insecticides generally do not share their properties of extreme environmental persistence and ability to bioaccumulate. Therefore our interest and concern with insecticides centred principally on their immediate toxic effects on terrestrial and aquatic invertebrates.

We did not, however, ignore other types of pesticide fungicides, growth regulators, desiccants, algicides, rodenticides, acaricides, nematicides, soil sterilants and animal repellents were reviewed separately (Hanson & Davis 1988). With the exception of fungicides, these other types of pesticide are not used in sufficient quantity to cause much concern and/or are not used in ways that might significantly damage wild fauna or flora via drift. Some of these groups, eg rodenticides, do cause concern but not because of drift.

Table 7.1 Sensitivity of aquatic invertebrates (three crustaceans, one plecopteran) to insecticides, compared with the sensitivity of rainbow trout. The insecticides are listed in Ivens (1992). LC_{50} (invertebrate)/LC_{50} (trout) in static 96 h tests. + = up to 10 times more sensitive than trout, ++ = 10-100 times more sensitive, +++ = more than 100 times as sensitive; < = up to 10 times less sensitive, etc ( ) refers to a different species of the genus. From Johnson & Finley (1980), collated by Williams *et al* (1987).

Compound	*Asellus brevicaudus*	*Daphnia pulex*	*Gammarus fasciatus*	*Pteronarcys californica*
Azinphos-methyl	<		++	+
Carbaryl	+	+++	++	+++
Chlorpyrifos			(++)	<
Derris (Rotenone)		<<<	<<	
Dimethoate			(++)	+++
Endosulfan			(<)	<
Fenitrothion		+++	+++	+++
Gamma-HCH (Lindane)	+	<<	+	+
Methomyl		+++		
Oxydemeton-methyl	+		+	
Trichlorphon		+++	(++)	++

Fungicides, however, are used on a huge scale; they are, for instance, the most widely used type of pesticide applied from the air, a method of application that can lead to significant levels of drift occurring over a hundred metres away from its source (Chapters 3, 5 and 6). Concerns include effects on non-target fungi or on the fungal components of lichens. There appear to be little or no data on either topic (eg see Brown 1992) and both may merit some attention in the future. Certain fungicides are also known to be toxic to earthworms (eg benomyl) or to insects (eg pyrazophos). However, because of the more overt hazards presented by herbicides and insecticides, it was decided to concentrate the experimental work on these pesticide groups.

In deciding which herbicides and insecticides to study, factors considered included degree of toxicity, spectrum of activity and scale of use. Vapour drift damage by herbicides was a topic shrouded in mystery and we needed to know whether it was important for us and, if so, how we could understand it better.

7.2.2 Types of application and theoretical safe distances

The impact of spray drift in part depends on the (toxic) properties of the pesticide and on the extent of drift.

As discussed in Chapter 1, a wide variety of factors affect the extent of spray drift, including method of application (refer to Figures 1.1 and 1.3 for examples). For herbicides, although sensitive species of plants may be affected by less than 1% of the field application rate (Elliott & Wilson 1983), it seems that if deposits are not allowed to rise above 1% of the field application rate, then serious acute effects on natural vegetation

may usually be avoided. Based on this 1% level, it was possible to calculate, following the initial contract review (Williams *et al* 1987), provisional 'safe distances' for different types of spraying. For instance, hydraulic spraying by tractor at wind speeds 1-2 on the Beaufort scale would have an estimated safe distance of 10 m (ie plants at least 10 m away should avoid serious acute effects), while for hydraulic spraying from the air the distance was 250 m. This resulted in advice to NCC staff to beware, during pre-spray consultations with aerial spraying contractors, of any new spraying developments within 250 m of an SSSI. Coincidentally 250 m had been the distance adopted by Regulatory Authorities when recommending that pyrethroids should be kept from water courses when sprayed from the air (eg see Ivens 1992). The theoretical safe distances were therefore used to advise on the extent of buffer zones needed on the ground to protect sensitive sites.

7.2.3 Bioassays, other tests and buffer zone estimation

The main part of the work centred on bioassay studies in which test plants or invertebrates were exposed at varying distances from herbicide or insecticide sources respectively or to varying dose levels. In many tests, plants were exposed individually, species being chosen to be representative of families or plants of a certain structure (see Chapter 2, spray drift dose response; Chapter 3, experiment 1). Other work included long-term effects on microcosm communities (Chapter 3, experiment 3) and impacts on seedlings (Chapter 3, experiments 4-7), on lichens (Chapter 4) and on ferns. Work on ferns focused on monitoring the effects of the herbicide asulam. This was done in part using *Rumex acetosa* as a higher plant indicator of what might happen to ferns, which may be of similar sensitivity (Chapter 3). However, ferns were also directly treated with asulam; these trials were not reported in earlier chapters, but observations on two species are summarised in Table 7.2. This, together with earlier work (Horrill *et al* 1978), indicated ferns to be sensitive to levels of asulam well below those required to control bracken. Thus rare ferns close to and especially within sprayed areas are at great risk (see also later in this Chapter). For ground spraying with a tractor-mounted, hydraulic sprayer, a safe distance of 10 m for good weather conditions may be adequate (ie it should avoid deposition on the sensitive species at >1% of the rate used against bracken).

Table 7.2 Effect of asulam on regrowth of ferns. Ferns were treated in August 1988 and observed in July 1989. From Davis *et al* (1990).

		Number of plants with new fronds			
Species	**Dosage ***	**Healthy**	**Unhealthy**	**Dead**	**None**
Dryopteris filix-mas	Control	7	-	-	3
	½ Standard	-	2	2	6
	Standard	1	-	3	6
Polypodium vulgare	Control	6	-	-	4
	½ Standard	-	-	-	10
	Standard	-	-	-	10

* Standard dosage equivalent to 11 litres Asulox per hectare

Bioassay tests with invertebrates have utilised terrestrial and freshwater indicator species. Additionally, one experiment was undertaken on the impact of drift of demeton-s-methyl on arthropods living in hedges next to arable fields (Greig-Smith *et al* 1992). Insect

populations suffered immediate reductions but quickly recovered, probably because of reinvasion from adjacent unsprayed areas.

In this Chapter, it is worth briefly reviewing the rationale behind the bioassays. As stated above, the initial aim was to identify situations that gave the most concern as regards drift impacts. Bioassays were then undertaken under typical conditions or under worst case conditions. We needed to know the range of effects that might occur in the field. This included studies done on commercial operations under conditions when, strictly, spraying should not have taken place (Chapter 3, section 3.3). The primary objective of bioassay work was to determine the extent of safe distances needed to protect sensitive animals and plants. These would then be used to set buffer zones of appropriate width around sensitive sites. Different views of what levels of damage are acceptable are likely to lead to different estimates of buffer zones derived from the same set of data. We have seen above that insecticide drift can affect populations of insects in boundary hedges, but that recoveries can be swift if recolonisation is possible. Does it therefore matter if, for instance, individual invertebrates are killed on reserves (especially if they are not noticed), providing populations are unaffected in the long term? This subject is included for consideration in our current contract on aerial drift, to be completed by 1994. With the invertebrate studies reported here, it is acknowledged that some mortality (eg 10%) may be acceptable in deriving buffers (Chapters 5 and 6; see also Payne *et al* 1988). When recommending buffers for freshwater invertebrates, there are the additional factors of depth of water and presence or absence of sediment to be taken into account. However, there are two other factors which might lead to buffers being underestimated. First, there could be sublethal effects or delayed mortality that will not be revealed by these acute studies. Secondly, buffer calculations are based on the reactions of one or a small number of indicator species, and there is no reason to suppose that these are the most sensitive species of all. So our approach to date has been a pragmatic one of deriving buffers that should prevent serious acute effects.

With plants, the question of acceptability is somewhat different. Conservationists are unlikely to find acceptable any damage that can definitely be attributed to pesticide drift (although damaged plants may recover). Plants do not possess the power of rapid recolonisation, as displayed by some invertebrates. But in field situations it may not be possible to differentiate symptoms of herbicide damage from those of other factors, such as extreme weather conditions or other air pollutants.

For ground spraying, buffers have been based on different approaches (eg 10% reduction in shoot dry weight in Chapter 2 or shifts in flowering performance, seed production and seed viability in the microcosm experiment in Chapter 3). This work indicated that a relatively narrow buffer of 10 m protects mature plants in nearly all situations, although seedlings may be more sensitive. For aerial spraying of asulam, the buffer in a worst case situation was based on 'damage' not being significantly worse than on control plants. Further work is in progress on the aerial spraying of asulam. In the meantime the computed buffer of 161 m should be regarded as the maximum required; reductions might be allowed depending on local conditions. Thus, for asulam, the original general safe distance of 250 m, based on avoiding a deposition rate of 1%, is seen to be rather too great. Some information is given in Chapter 5 about how wind speed can modify impact (of an insecticide in that example).

Table 7.3 summarises the buffer zones indicated by the experiments reported in the preceding Chapters. Not surprisingly, larger buffers are needed for aerial spraying than for hydraulic spraying from the ground, with air-assisted orchard spraying intermediate. On the evidence to hand, larger buffers are required for the insecticides tested than for the herbicides (see also Section 1.9). For herbicides, safe distances were similar to those

predicted by the initial desk study (Williams *et al* 1987). For ground spraying with insecticides, however, they were rather greater than first predicted. Predictions had been based on avoiding a deposition rate of >1% of target field rate, but experiments with the chitin inhibitor diflubenzuron showed that with particularly toxic insecticides/sensitive insects this threshold was insufficient. In Figure 7.1, mortality of bioassay caterpillars was 90-100% even at about 1% of target field rate. Deposition needed to be much less than 1% for effects to be avoided. For diflubenzuron, Davis *et al* (1991) estimated that a buffer zone of 32 m might be needed in some circumstances.

Table 7.3 Buffer zones recommended in this book, listed in order of ascending size

Chapter	Pesticide	Application from ground or air	Species at risk	Buffer zone (m)
4	Herbicides	Ground	Heathland lichens	0
4	Herbicides	Ground	Pasture woodland lichens	0, but avoid direct spraying
3	Herbicides	Ground	Established higher plants	10
2	Herbicides	Ground	Higher plants	10 except for glyphosate with some species
3	Herbicides	Ground	Seedling higher plants	Up to 20
5	Insecticides	Ground	Terrestrial invertebrates	12-24
6	Cypermethrin	Ground	Aquatic invertebrates	28
5	Insecticides	Ground (orchard air-assisted)	Terrestrial invertebrates	50
3	Asulam	Air	Ferns	Up to 161
6	Deltamethrin	Air*	Aquatic invertebrates	180
5	Deltamethrin	Air*	Terrestrial invertebrates	>250

* Stable conditions

The trial with aerial spraying of deltamethrin was done under unusually stable conditions. While it may be regarded as a worst case, it does indicate a worrying potential for insecticides to kill more than 100 m from the target crop. Because of this concern, work on the aerial spraying of insecticides is continuing, including with narrower spectrum insecticides under more typical weather conditions.

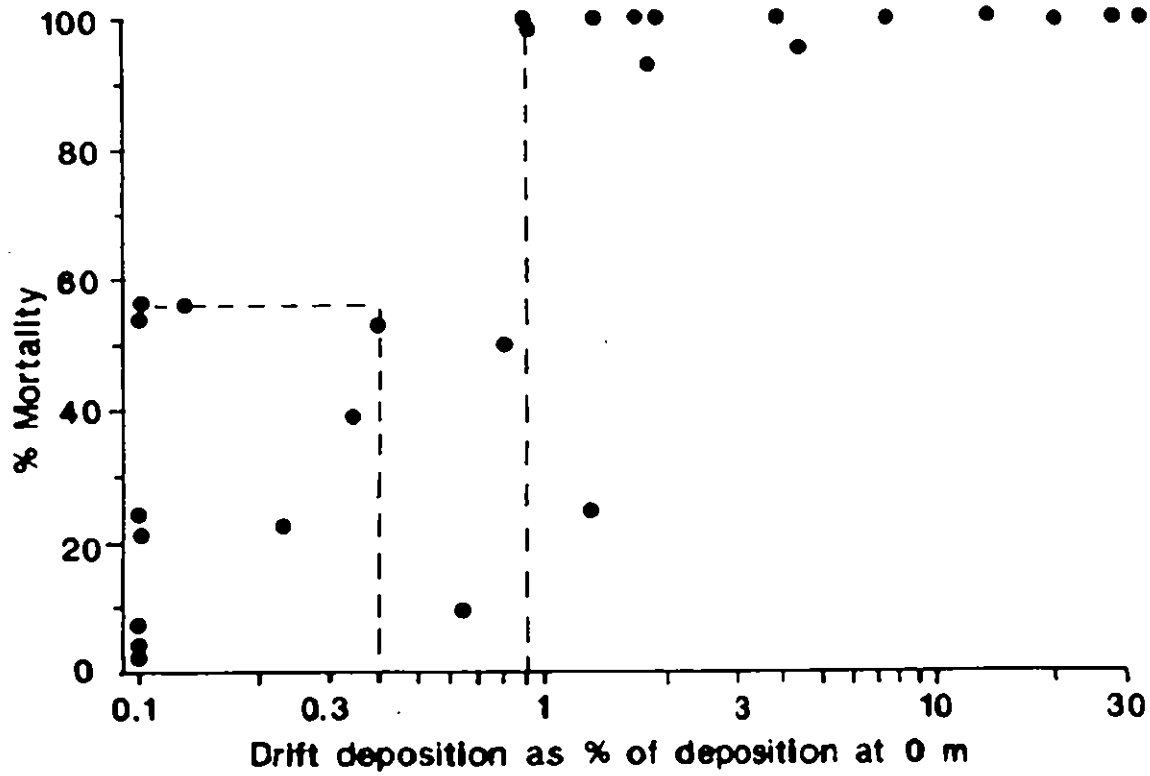

Figure 7.1 The relationship between percentage mortality of *Pieris brassicae* caterpillar and diflubenzuron drift deposition in five bioassay trials. From Davis *et al* (1991).

Just because our experiments have concentrated on plants and invertebrates, it should not be assumed that other organisms are safe from the impact of spray drift. Ernst *et al* (1991) described how aerial application of endosulfan caused unacceptable mortality of fish 200 m away. Endosulfan is not approved for aerial use in Britain.

7.3 Potential impacts and how to avoid them

7.3.1 Pesticide use inside SSSIs

Inside SSSIs, pesticide use for conservation reasons should be minimal and be more or less restricted to herbicides (Cooke 1986, 1991). The targets are likely to be single plant species invading open habitats. The rationale behind a decision to use a herbicide is to control the invasive species while not affecting the remainder of the community. This is achieved by using relatively specific herbicides and/or by employing precise placement techniques, such as application via paint brush or wick-wiper. Broad spectrum herbicides should only be sprayed in situations where non-target flora will be unaffected, eg against extensive monocultures of the invasive species. In such situations the appropriate buffer should be applied (eg 10 m; Table 7.3).

Nevertheless there are conservation applications of concern from the point of view of drift. For instance, bracken control by asulam is one of the more frequent herbicide uses on reserves (Cooke 1991). Asulam is approved for use from the ground at very/ultra low volume from an ULVA 8 high speed rotary atomiser. This device produces driftable droplets and relies on wind and turbulence to disperse them downwind and impact them

on target vegetation. The Forestry Commission recommends a buffer zone of 100 m to protect susceptible forestry crops (Williamson & Lane 1989). It therefore follows that such a sprayer should not be used for conservation purposes within 100 m of rare ferns. The low speed rotary atomizer, the Herbi, is also used to spray asulam to control bracken. Williams *et al* (1987) pointed out that such equipment was much less drift-free than was popularly supposed. Whereas conventional hydraulic equipment typically gives a spray deposit of about 1% of emission at 10 m (Williams *et al* 1987), a Micron Herbi was found to give about 5% at this distance (Lake *et al* 1976). This suggests that a buffer of several tens of metres is required for a Herbi.

In addition to occasional use of herbicides on SSSIs for conservation purposes, owners or occupiers will more often wish to employ herbicides for other purposes. For instance, thistles *Cirsium* spp. frequently need controlling on grassland SSSIs. Any herbicide which kills thistles can be expected to affect a range of exposed non-target flora. Such a herbicide should of course never be sprayed on floristically-rich grassland. On impoverished fields where there are adjacent areas of floristic importance (eg ditches or other fields) it may be possible to agree to spraying, providing an appropriate buffer is left (refer to Table 7.3 or elsewhere in this book). The buffers refer to downwind distances, so that if sensitive sites are upwind, utilising a buffer should confer an extra element of safety. However, the sensitivity of the floristic interest should be emphasised to the operator in advance, to avoid spraying in unsuitable conditions ie with a strong wind blowing towards areas of interest.

Deposits resulting from vapour drift cannot be quantified with any confidence (Chapter 2); damage occasionally occurs over great distances. However, some active ingredients are more prone to drift in the vapour phase. Care should be taken with these to ensure that vapour drift does not damage the floristic interest inside, or even outside, the SSSI. The products Garlon 2 and 4 contain the active ingredient triclopyr (in ester form), which is known to be prone to vapour drift. *The UK Pesticide Guide 1992* warns "Avoid spray drift onto edible crops, ornamental plants, Douglas fir, larches or pines. Vapour drift may occur under hot conditions" (Ivens 1992). Following an incident on an SSSI in 1990, advice was sought from Dr V Breeze. As a consequence it was recommended to NCC's regional staff that Garlon formulations should not be used on days when the air temperature had reached or was likely to reach 15°C. This would seem to be good advice for any herbicide which has been implicated in vapour drift incidents; such herbicides include ester-based formulations in particular.

7.3.2 Pesticide use close to SSSIs

Ground spraying If ground spraying takes place next to an SSSI the species at greatest immediate risk seem to be plants and terrestrial and aquatic invertebrates. If spraying has been done regularly for a number of years, it is likely that there has been some modification of the plant and/or animal communities on the extreme edge of the SSSI. However, it may be difficult to ascribe any impact to pesticide use because of the many other environmental factors influencing the biota - some of which may have similar effects. If there is concern, it may be possible to detect the characteristic epinastic twisting and elongating of foliage caused by auxin herbicides or dead surface-breathing invertebrates in ponds as a result of recent insecticide drift. The use of water-sensitive paper to detect drift droplets can help to confirm such concerns. But it may be of greater concern when there are plans to spray next to a sensitive reserve previously unexposed to potentially damaging drift. In such cases it may be possible to negotiate a buffer or to agree to spray only in certain weather conditions, which will minimise drift into the SSSI. In Environmentally Sensitive Areas or through set aside, there may be opportunities to locate uncultivated strips in strategic positions.

As was seen in Chapter 5, a hedge with appropriate height and porosity can provide a degree of shelter from the effects of pesticide drift. An example of the way in which a hedge reduced damage of MCPA drift to young plants of ragged-robin *Lychnis flos-cuculi* is shown in Figure 7.2.

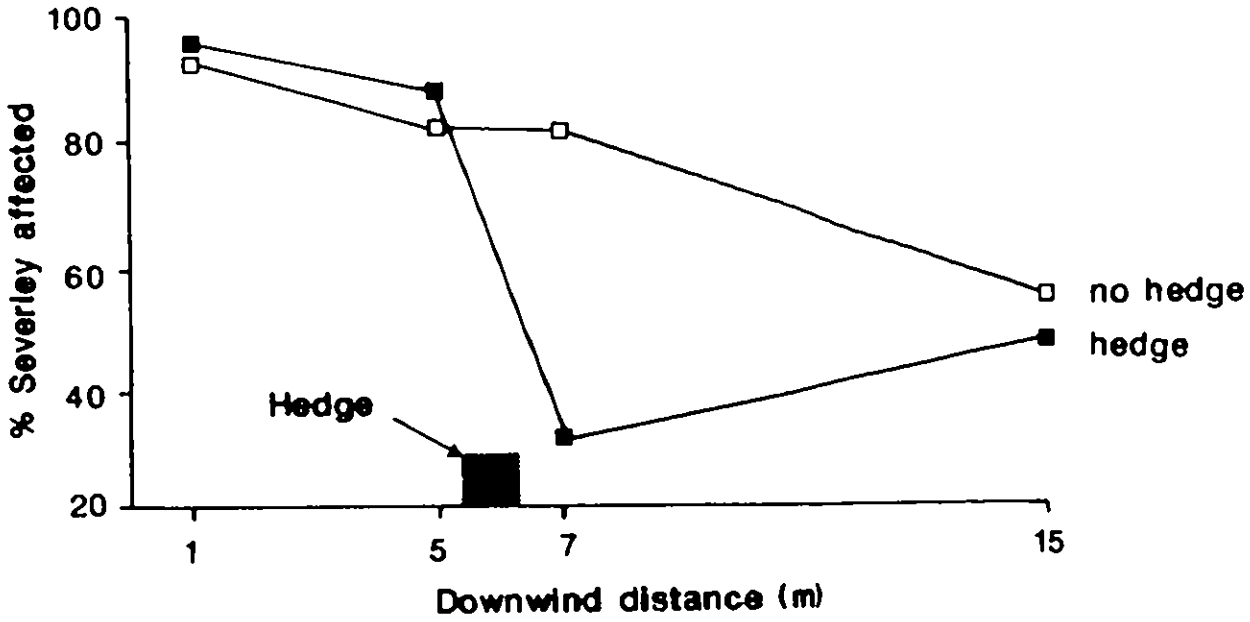

Figure 7.2 Bioassay results for ragged-robin *Lychnis flos-cuculi* receiving MCPA drift in relation to a hedge located at 6 m (solid symbols) or a gap in the hedge (open symbols). From Davis *et al* (1992).

Penetration of drift into a woodland edge has also been measured (Davis *et al* 1992). Comparisons between drift of water droplets into a woodland NNR and drift of insecticide in open arable habitat showed no significant reduction in the wood (Figure 7.3). This woodland edge was not particularly open and the results may suggest that effects on flora and fauna can occur in the edge of woods, and indeed other habitats, where they abut cropped land.

Aerial spraying There is a requirement stemming from the Control of Pesticides Regulations 1986 that NCC's successor country agencies should be consulted at least 72 hours in advance if land is to be sprayed from the air within ¾ of a nautical mile of an SSSI. This provides regional staff with an opportunity to express concerns to the spray operator. Areas of greatest concern will be situations in which damage has been suspected in the past, and SSSIs that have not previously been exposed to this type of risk from drift. The latter situation, for example, would occur if a farmer near an SSSI switched from growing cereals to peas and decided that summer insecticides needed to be applied from the air. There is a requirement in the Regulations for operators to ensure that only the target area is treated. Evidence from drift trials (eg see Chapters 5 and 6) shows that in practice this may often be impossible, even if a certain amount of drift is allowed for.

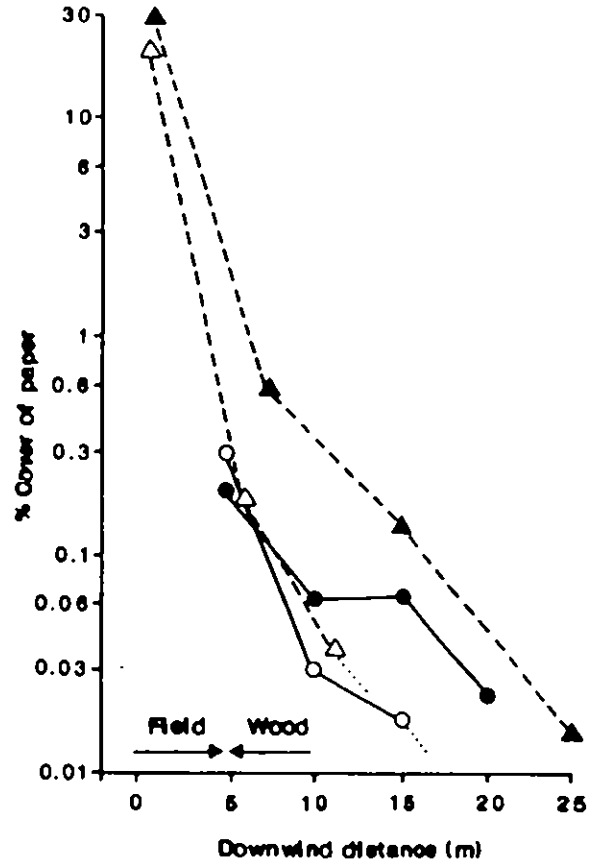

Figure 7.3 Water spray drift into a woodland edge: drift deposition (percent cover) on water-sensitive papers with the sprayer 5 m from the edge of the wood (two trials: open and solid circles). Insecticide drift from farm fields is shown for comparison (open and solid triangles). From Davis *et al* (1992).

Again, it is drift from insecticides and herbicides that is likely to be of the greatest immediate concern. The area treated from the air has generally decreased during the 1980s and this is particularly true for insecticides, which have decreased from 149,000 ha treated in 1984 to 13,000 in 1990 (Thomas & King 1992). Herbicide use from the air has always been relatively minor and the total has changed little, with 6,900 ha treated in 1984 and 5,800 ha in 1990 (Thomas & King 1992). During that time asulam use has increased from 1,000 ha (Longland & Chapman 1986) to nearly 5,800 ha. Asulam can be applied in the form of larger droplets, so that the extent of drift from aerial application of asulam may be less than that with insecticides. There was negligible use of other herbicides in 1990.

Insecticides (and other pesticides) being applied from the air must be approved specifically for that purpose (as listed in MAFF/HSE 1992; Ivens 1992). Also label conditions must be adhered to; for instance pyrethroids, if approved for aerial application, should not be sprayed from the air within 250 m of a water body, which includes water on SSSIs (eg alpha-cypermethrin; Ivens 1992).

During a pre-spray consultation, the operator can be advised of ways of minimising risk to the SSSI. If reasonable advice is disregarded and damage to the SSSI results, an offence may have been committed. For asulam at least, detection of droplets on water-sensitive papers may be taken to indicate that levels sufficient to damage sensitive species have been deposited on the SSSI (Marrs *et al* 1992). However, it is of course preferable to avoid damage rather than prove later that it has occurred. In practice, it should be possible to resolve any differences prior to spraying, perhaps by involving the Health and Safety Executive. When large-scale programmes are planned in or near sensitive areas, general guidelines should preferably be agreed by all interested parties well in advance. Thus the Code of Practice for bracken control in the Peak District National Park stipulates buffers for different types of spraying, including 160 m for hydraulic systems from the air (C Edwards personal communication).

One objective of the current contract on aerial spraying is to determine which insecticides can be safely sprayed beside an SSSI without a buffer, which need a buffer and which appear to be too dangerous to be approved for aerial use. The herbicide asulam is clearly in the intermediate category and further information on its buffer requirements are being determined. It will clarify the situation considerably if the necessary buffers can be specified as conditions of approval. This has already been done for fenitrothion, when used from the air to control insect pests in forests. With the continuing reduction in the amount of aerial spraying, there will be relatively few occasions when operators find they are within ¾ nautical mile of an SSSI. However, it is important that the potential for problems is appreciated and understood and that damage can be prevented on the occasions that it might occur.

So far, nothing has been said about overspraying from the air. Because of the relatively fast forward speed of helicopters and fixed-wing aircraft, failure to switch off before or at the edge of the crop could lead to overspraying. Figure 7.4 shows a patch of bracken sprayed from the air with asulam and whether bioassay plants suffered damage in different locations, each 20 m from the edge of the patch. Plants at most of the downwind locations were damaged, as were several away from the downwind edge. Damage to the latter group appeared to have resulted from turbulence effects and/or from overspraying (Marrs *et al* 1990; R Marrs pers. comm.). Overspraying should be avoided by asking for the flight path to be parallel to the boundary of the SSSI, if possible.

7.3.3 Pesticides and the wider countryside

This programme of work has documented the effects of herbicides and insecticides in particular on our flora and fauna respectively. While some effects might have been predicted, others have been surprising. Thus relatively few species in the plant microcosm test (Chapter 3, experiment 3) were affected even right under the sprayer; many established perennial plants appear to be able to withstand herbicide damage and can recover quickly if necessary. On the other hand, the effects caused by deltamethrin sprayed from the air (Chapters 5 and 6) indicated how surprisingly extensive effects can be under stable atmospheric conditions. The overriding conclusion from the work is that pesticides can, via drift, cause measurable damage to wildlife species and habitats and that the extent of effects is not always predictable. We have tried to define buffer zones that take account of an element of unpredictability. Users in the wider countryside should therefore be encouraged to protect, by means of buffers, sensitive wildlife habitat such as water courses, ponds, hedges, woods etc. Because of the exponential fall-off in the amount of drift, the establishment of a buffer of any size will bring benefits, although not necessarily complete protection. Thus the conservation headland approach of the

Game Conservancy Trust will help to protect plants and invertebrates in boundary hedges (Cuthbertson & Jepson 1988).

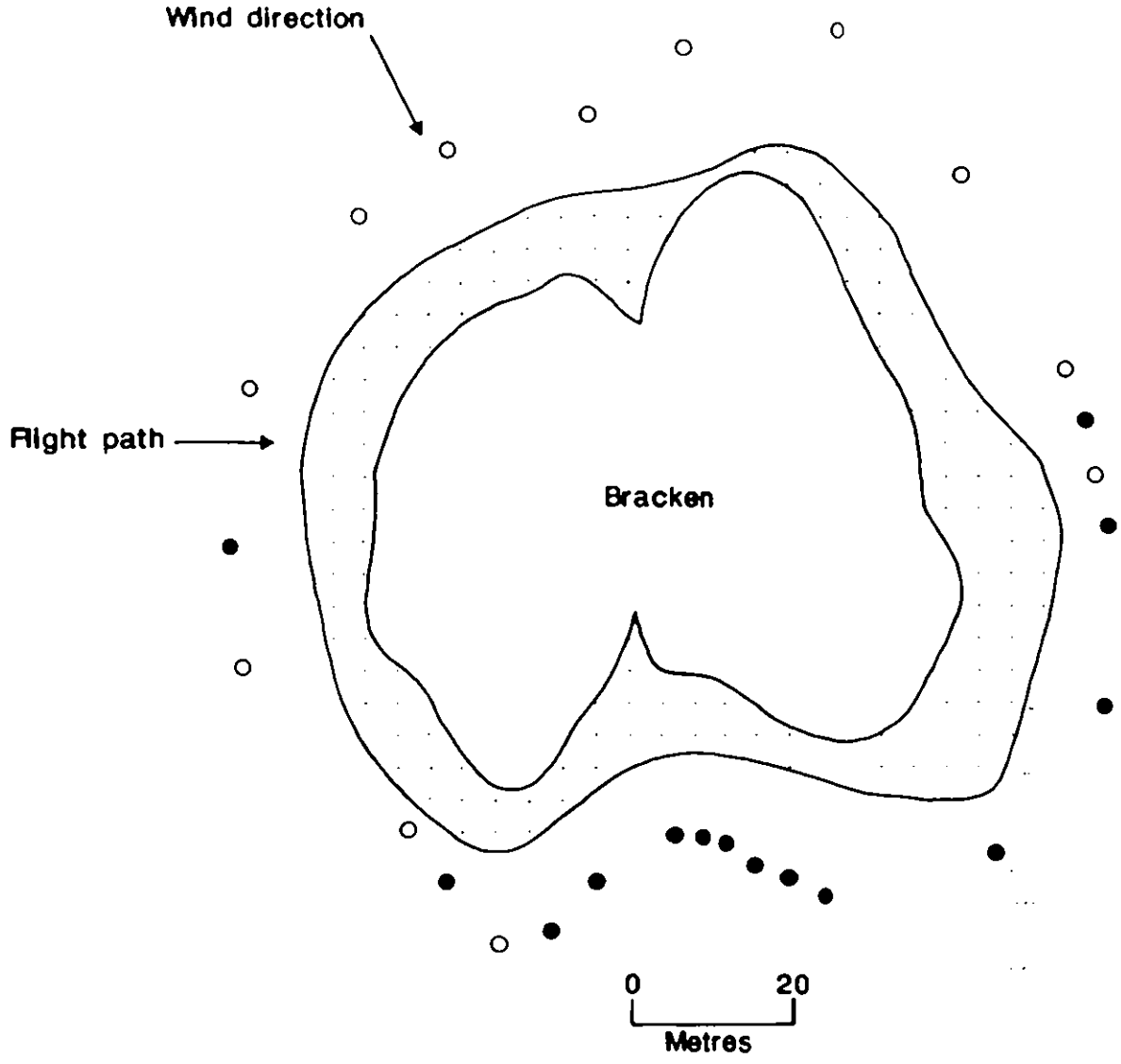

Figure 7.4 Aerial spraying of asulam to control a small patch of bracken. The area is stippled outside the patch where deposition was 10% or more of that recorded inside the patch (as measured with water-sensitive papers). Locations where damage was noted on bioassay plants at a distance of 20 m are marked with a solid circle. Where no damage was recorded an open circle is used. From Marrs *et al* (1990).

Current labelling and pesticide literature sometimes include phrases about drift. Labels of certain herbicides, eg dichlorprop, MCPA, mecoprop, draw attention to the need to avoid damage to "nearby susceptible crops" (Ivens 1992). For other herbicides (eg thifensulfuron-methyl), the need to avoid contamination of water is emphasised, sometimes with buffers being given (hexazinone, triclopyr). For insecticides, the focus is again on protection of water, often with statutory buffer zones. Thus alpha-cypermethrin should not be sprayed from the air within 250 m of any watercourse. Phrases are being introduced to avoid overspraying of water; for lambda-cyhalothrin, users are advised: "Do not allow spray from vehicle-mounted sprayers to fall within 6 m of surface waters or

ditches, or from hand-held sprayers within 2 m; direct spray away from water" (Ivens 1992). The pyrethroid fenpropathrin is approved for use from air-assisted sprayers and is specially toxic to freshwater life: "Do not operate air-assisted sprayers within 80 m of surface water or ditches, other wheeled sprayers within 6 m, hand-held sprayers within 2 m and direct spray away from water" (Ivens 1992).

Some of these precautionary phrases are relatively new and all are most welcome. However, there is a need to introduce a consistency to the phraseology and to encourage protection for other features of the environment. Some evaluation is also needed on the degree to which the precautionary phrases are acted upon by users.

7.4 Conclusions

Considering the level of concern over the last three decades about the impact of pesticides on wildlife, there have been remarkably few studies that have focused specifically on determining the effects of drift, as opposed to the extent of drift (see Appendix 2). The total number of relevant articles of which we are aware and that we have quoted in these pages does not reach double figures. Such papers tend to report specific situations that have been identified as of concern or interest. Our programme represents a more comprehensive approach to the issue. By its conclusion it will probably have increased the amount of literature on the topic several-fold (see Appendix 1). Although much of the experimental work has been straightforward, it answered crucial questions. Indeed it is a pity that such a programme was not undertaken years ago. In the past, the impact of drift may have been more severe, for example, because of the greater use of persistent organochlorines with a potential to bioaccumulate and because of more frequent aerial application.

The programme is not yet completed, but we felt that it was worth making more generally available the information presented at the Drift Seminar in 1992 (see Foreword). It is hoped that this book will increase awareness of the potential for pesticide drift to damage wildlife and its habitats, and will provide information on how such effects may be minimised.

7.5 References

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Appendix 5 Factors in a cost benefit analysis for pesticide withdrawal

FACTORS IN A COST BENEFIT ANALYSIS

The NERC has not undertaken a study into the costs and benefits of setting the pesticide MAC at any given value, but the aspects that should be considered are fairly clear. For an individual chemical or family group of chemicals, the cost of their continuing use should be assessed and set against the costs to agriculture and the agro-chemical business of their non use. The assumption being that the benefits are the reduction in costs associated with continued use. The factors that must be considered in calculating these two sets of costs are set out below.

CONTINUED PESTICIDE USE

a) Pesticide Residue Monitoring. If specific pesticides are in use then they have the potential to be present in food stuffs and drinking water. There is therefore the cost associated with the continued monitoring of all food and water destined for human consumption.

b) Human Health. There are few proven links between pesticide consumption through diet and deterioration in human health. Monitoring as described in a) should ensure this continues. However they may be very long term effects that might be shown to exist from continued exposure to very low levels and this potential cost can not be ignored.

c) Water Treatment. The only way to keep pesticide levels below the MAC in some supplies is by treatment (eg activated carbon filters). This cost is easy to quantify and indeed may not be too high at water treatment plants that may presently protect the supply of major conurbations. However, the cost of groundwater supplies may increase dramatically as they generally serve more local populations and currently receive minimal treatment.

d) Environmental Exposure. A great deal of expensive research is carried out into predicting the hazard resulting from the use of pesticides in the environment. This research needs to address both the toxic effect of chemicals to different biota and the likely levels these biota will experience in the environment. Assuming that pesticides do damage the environment it is very difficult to estimate the cost of such damage.

NON-USE OF PESTICIDES

a) Agriculture. The reduction in yield will need to be assessed with its implications for farmers' incomes and increased food prices. There are also implications for employment levels in rural areas.

b) Agrochemical Industry. A great deal of money is spent in developing new chemicals and the banning of a particular chemical therefore represents a wasted investment for the chemical industry.